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## THE MAGNETIC AND ELECTRICAL PROPERTIES OF FERROXCUBE MATERIALS

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*One of the most important results achieved from the scientific investigation of solids in the last decade is undoubtedly the development of ferromagnetic materials for use at high frequencies. Readers of this journal will already have gathered much about the application of these materials. An article devoted to this subject some years ago had of necessity to be relatively brief because the materials in question were then still in course of development. Now that this development work has been almost completed, it is possible to discuss these new ferromagnetic materials at greater length.*

### Introduction

The ferromagnetic materials to be dealt with in this article, and now known under the trade name of "Ferroxcube", arose from the need to avoid the losses occurring at high frequencies in the ferromagnetic metals hitherto commonly used. There are various physical causes of these losses, viz:

- 1) the occurrence of eddy currents,
- 2) the hysteresis phenomenon,
- 3) the so-called ferromagnetic resonance absorption<sup>1)</sup> and possibly other mechanisms.

The losses to be attributed to these causes are called the eddy-current losses, the hysteresis losses and the residual losses respectively.

The magnitude of the losses arising in the ferromagnetic core of a coil when a (weak) alternating current flows through it, is represented in practice by the so-called loss factor<sup>2)</sup>

$$\frac{\Delta R}{\mu_r f L},$$

where  $\Delta R$  is the equivalent resistance which (connected in series with the coil) would cause a loss equal to the losses arising from the ferromagnetic material,  $\mu_r$  is the relative magnetic permeability

of the ferromagnetic material ( $\mu = \mu_r \mu_0$ <sup>3)</sup>),  $f$  the frequency of the alternating current and  $L$  the inductance of the coil with core. In the case of a ring coil  $L = \mu_r L_0$ , where  $L_0$  is the inductance of the coil without core. The significance of the loss factor becomes clear when it is written in the form:

$$\frac{\Delta R}{\mu_r f L} = \frac{2\pi}{\mu_r} \frac{\Delta R}{\omega L} = \frac{2\pi}{\mu_r} \frac{1}{Q},$$

where  $Q$  represents the quality of a circuit with resistance  $\Delta R$  and inductance  $L$ . The factor  $1/\mu_r$  has been added because the loss factor so defined does not change when an air gap is introduced in the magnetic circuit.

For the known metallic ferromagnetics it is customary to write this loss factor in the following form:

$$\frac{\Delta R}{\mu_r f L} = C_e f + C_h B_{\max} + C_r, \quad \dots (1)$$

where  $C_e$  and  $C_h$  are constants, namely the eddy-current constant and the hysteresis constant. The term  $C_r$  represents the residual losses, which could be attributed to the causes mentioned under (3)

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1) See H. G. Beljers and J. L. Snoek, Philips Techn. Rev. 11, 313, 1949.

2) See J. L. Snoek, Philips Techn. Rev. 8, 353, 1946.

3) In the system of rationalized Giorgi units used here the permeability of vacuum is  $\mu_0 = 4\pi/10^7$  H/m and the dielectric constant of vacuum  $\epsilon_0 = 10^7/4\pi c^2$  F/m.



above.  $B_{\max}$  is the peak value of the magnetic induction. In a well-conducting ferro-magnetic material the eddy-current term appears to contribute by far the most to the loss factor at high frequencies, the more so since as a rule for use at high frequencies small values of  $B_{\max}$  suffice. For a plate of thickness  $D$  which is magnetized in a direction parallel to its plane, and assumed to be homogeneous and isotropic with respect to permeability, the eddy-current constant  $C_e$  assumes the following form:

$$C_e = \frac{\pi^2 \mu_0}{3} \frac{D^2}{\rho}, \dots \dots (2)$$

where  $\rho$  is the resistivity of the ferromagnetic material. It is seen that instead of using a solid core it is advantageous to build up the core from a large number ( $n$ ) of insulated thin plates with thickness  $D/n$ , which has led to the use of laminated cores. In fact, for a core with total thickness  $D$  constructed in this way the eddy-current constant is a factor  $1/n$  smaller than that for a solid core of the same material and the same dimensions. The higher the frequency for which the core is to be used, the thinner the laminations should be. Rolling very thin sheets, however, is an expensive process and therefore at high frequencies powder cores are used, consisting of minute, insulated particles with a diameter of about 5 microns. But the use of these powder cores has great disadvantages, since the core is not homogeneously filled with the ferromagnetic material. The magnetization is therefore not uniform throughout, and as a result there is a loss of "effective" permeability and the losses mentioned are increased<sup>4)</sup>.

These disadvantages led to the search for a ferro-magnetic core material with such a high specific resistance  $\rho$  as to make the eddy-current losses negligible (see eq. (2)), even when the material is used in a homogeneous form, i.e. neither laminated nor in powder form. For this reason ferromagnetic oxides have been developed, and those that are of technical importance have come to be known under the name of Ferroxcube. In conformity with the requirement for their development, these materials usually have such a high resistivity that the eddy-current losses become negligible. This does not imply, however, that no losses at all occur in Ferroxcube materials, but only that the losses which occur in them are mainly to be classified as hysteresis and residual losses. The residual losses (term

$C_r$  in eq. (1)) are a function of frequency (see note<sup>2)</sup>).

With a certain frequency and a certain maximum value of the induction it can be ascertained (for instance by measuring the hysteresis curve) what part of the total losses is due to hysteresis. It is not, however, possible — and this should be borne in mind right from the beginning — to apply this separation in such a general manner as is expressed in formula (1). If this formula were nevertheless applied to Ferroxcube materials it would be found that the coefficient  $C_h$  is also frequency dependent, whilst the term  $C_r$  depends on the induction as well as on the frequency. As will be shown farther on, however, the total loss arising from the ferromagnetic material can be expressed in a useful manner.

This article will now deal with the following points: the chemical composition and the crystallographic structure of the Ferroxcube materials and, in connection therewith, the saturation magnetization<sup>5)</sup>, which is of fundamental importance for the ferromagnetism; the behaviour of Ferroxcube materials in weak fields, attention being directed to the magnetic losses and permeability (also as a function of temperature), which is of the utmost importance for practical applications; the behaviour of these materials in strong fields, attention again being paid to permeability and losses. Finally something will be said about the exceptional dielectric properties of Ferroxcube materials which under certain circumstances may lead to additional losses.

### Composition and preparation of the ferrites

As far as their chemical composition is concerned Ferroxcube materials belong to the group of ferrites with the composition  $\text{Me}^{2+}\text{Fe}_2^3\text{O}_4$ , where  $\text{Me}^{2+}$  is a symbol for a divalent metal. In particular all Ferroxcube materials are cubic ferrites, with the same crystal structure as  $\text{Fe}_3\text{O}_4$ , which is also the structure of the mineral spinel ( $\text{MgAl}_2\text{O}_4$ ) and is therefore called the spinel structure<sup>6)</sup>. Ferrites

<sup>4)</sup> See the article quoted in note<sup>2)</sup>. — When the particles are very small also the "intrinsic" permeability of the particles is smaller; see L. Néel, C. R. Paris 224, 1550, 1947.

<sup>5)</sup> As is presumably known, a ferromagnetic material in the non-saturated state is divided into Weiss domains. Within each domain the material is spontaneously magnetized and the order of magnetization equals the saturation magnetization corresponding to the temperature in question. The fact that the magnetization of the material as a whole differs from the saturation magnetization is due to the differences in direction of the magnetization in the various domains. The term saturation magnetization, without any further definition, is to be understood here as the value of the magnetization in sufficiently strong fields at a temperature of 0 °K; it is thus equal to the spontaneous magnetization at that temperature. (The values quoted in this article are those measured at the temperature of liquid nitrogen, but the resultant error is not of great consequence.)

<sup>6)</sup> See also: E. J. W. Verwey, P. W. Haaijman and E. L. Heilman, Philips Techn. Rev. 9, 185, 1947.



may be imagined as being derived from  $\text{Fe}_3\text{O}_4$  by replacing the divalent ferrous ions by one or more divalent metal ions, e.g. Mn, Co, Ni, Cu, Mg, Zn or Cd.

Ferrites are usually prepared by a sintering process such as commonly employed in the ceramic industry. The component metal oxides are mixed, ground, usually pre-sintered and ground again, finally compressed into the desired shape with the necessary binders and sintered at a high temperature. This sintering is accompanied by a certain amount of shrinkage, which has to be allowed for when determining the dimensions of the mould. In the final sintering process the atmosphere plays a large part in determining the degree of oxidation of the product, which is of great importance. It is also pointed out that this sintering process does not yield an absolutely solid material but a product containing a small volume percentage of voids.

### Crystal structure of the ferrites

As already remarked, Ferroxcube materials with the chemical composition  $\text{Me}^{2+}\text{Fe}_2^{3+}\text{O}_4$  crystallize with the spinel structure. This structure may be described as follows (see fig. 1). The large oxygen

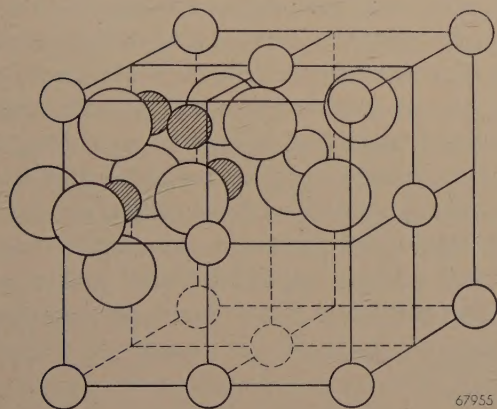


Fig. 1. The unit cell of the spinel lattice. The large spheres are oxygen ions, the small hatched spheres ions in octahedral sites, the small non-hatched spheres ions in tetrahedral sites. Only in two of the eight octants forming the unit cell have all the ions been drawn. There are twice as many ions in octahedral sites as in the tetrahedral ones.

ions form, to a very good approximation, a cubic close-packed structure of spheres. The small divalent and trivalent metal ions are found in the small interstices between the large oxygen ions. In a close packing of spheres there are two kinds of interstices, one being surrounded by four oxygen ions, the so-called tetrahedral sites, the other by six oxygen ions, the octahedral sites. In the spinel structure twice as many octahedral

as tetrahedral sites are occupied. A very important point is the distribution of the various metal ions among the crystallographic sites available. The fact that there are several possibilities in regard to this distribution was first demonstrated by Barth and Posnjak <sup>7</sup>). This was further investigated in connection with ferrites by Verwey and Heilmann <sup>8</sup>), with the following result:

In the case of the so-called "normal" spinels the divalent metal ions occupy the tetrahedral sites, whilst all octahedral sites are occupied by the trivalent metal ions. This arrangement is found, with some minor deviations, for Zn and Cd ferrites. All other known simple ferrites (those containing only one kind of divalent metal ions) are said to be inverted, since the divalent metal ions are situated entirely (or mainly) in octahedral sites, while the trivalent ions occupy for one half the remaining octahedral sites and for the other half the tetrahedral sites.

### Saturation magnetization

#### Single ferrites

The value of the spontaneous magnetization (saturation magnetization) differs for the various ferrites. It is zero for zinc and cadmium ferrites, i.e. these two ferrites (the only simple ferrites which are not inverted; see above!) are not ferromagnetic. All other ferrites are ferromagnetic.

It has now been found that the value of the saturation magnetization of Ferroxcube materials can be related to the crystal structure described, in particular to the distribution of the ions among the two crystallographic sites available in the spinel lattice.

It should first be mentioned that for the ferromagnetic metals it has hitherto not been possible to derive a theoretically calculated value for the saturation magnetization agreeing with the values found. For ionic compounds such as those with which we are concerned here, one would in principle expect this to be possible, since it is known that in paramagnetic salts in which the same ions occur a certain magnetic moment can be ascribed to each ion. It is reasonable to assume that the magnetic moment of a certain ion in a ferromagnetic ionic compound, in our case a ferrite, is equal to that in a paramagnetic salt. Assuming, moreover, that all magnetic ions fully contribute towards the magnetization (i.e. that at a temperature of 0°K the magnetic

<sup>7</sup>) T. F. W. Barth and E. Posnjak, Z. Krist. **82**, 325, 1932.

<sup>8</sup>) E. J. W. Verwey and E. L. Heilmann, J. chem. Phys. **15**, 174, 1947.



moments of all ions are parallel), it should be possible to calculate the saturation magnetization of our ferrite expressed in Bohr magnetons per "molecule"  $\text{Me}^{2+}\text{Fe}_2^{3+}\text{O}_4$  by adding the moments of the ions present.

The values found experimentally, however, are much smaller than those obtained by such a calculation; see table I, columns 4 and 6.

Table I. The magnetic moments of various ferrites at saturation  $M_s$ , expressed in the number of Bohr magnetons per molecule<sup>9)</sup>.

Ferrite	Ions in tetrahedral sites	Ions in octahedral sites	$M_{s_{\text{oct.}}} + M_{s_{\text{tetr.}}}$	$M_{s_{\text{oct.}}} - M_{s_{\text{tetr.}}}$	$M_{s_{\text{exp.}}}$
ferrous ferrite	$\text{Fe}^{3+}$	$(\text{Fe}^{2+}\text{Fe}^{3+})$	$(4+5)+5=14$	$(4+5)-5=4$	4.2
manganese ferrite	$\text{Fe}^{3+}$	$(\text{Mn}^{2+}\text{Fe}^{3+})$	$(5+5)+5=15$	$(5+5)-5=5$	5.0
nickel ferrite	$\text{Fe}^{3+}$	$(\text{Ni}^{2+}\text{Fe}^{3+})$	$(2+5)+5=12$	$(2+5)-5=2$	2.3
zinc ferrite	$\text{Zn}^{2+}$	$(\text{Fe}^{3+}\text{Fe}^{3+})$	$(5+5)+0=10$	$(5+5)-0=10$	0
Column 1	2	3	4	5	6

The explanation for this discrepancy has been given by Néel<sup>10)</sup>, who assumes that a magnetic dipole on a tetrahedral site has a strong tendency to align itself in anti-parallel orientation to the dipoles in adjacent octahedral sites. A similar, through less pronounced, interaction takes place also between magnetic moments in one and the same kind of lattice site.

These assumptions have, among others, the following consequences<sup>11)</sup>:

The magnetic moments in sites of one kind have parallel orientation and the total magnetization of the ions in the octahedral sites is anti-parallel to that of the ions in the tetrahedral sites, since all "tetrahedral neighbours" of a certain "octahedral moment" will be anti-parallel to that moment. All octahedral neighbours of the tetrahedral moments will in turn be anti-parallel to the latter, i.e. they will be parallel to the dipole in the octahedral site considered first, and so on. The magnetization of the whole domain will therefore be equal to the difference of the partial magnetizations of the dipoles in the octahedral and the tetrahedral sites, this being approximately in agreement with the values found experimentally (table I, columns 5 and 6).

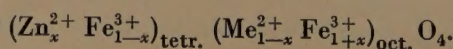
Special consideration has to be given to cases such as, for instance, that of zinc ferrite, where the tetrahedral sites are exclusively occupied by non-magnetic Zn ions. Here no interaction can occur between magnetic moments on different lattice sites, such as governs the situation described above. The only magnetic interaction likely to occur in this case is that between the ferric ions

in the octahedral sites themselves. Such an interaction tends to make the number of anti-parallel pairs of neighbours as large as possible. If each magnetic moment has only anti-parallel nearest neighbours then the apparent total magnetization will be zero, as is indeed found to be the case with zinc ferrite. For the complicated spinel lattice, it is true, it is not easy to imagine a condition where all the nearest neighbours of an ion have moments anti-parallel to it. Yet here, too, an arrangement is feasible whereby the total magnetization is zero. The resulting moment will of course also be zero if the interaction between the ferric ions in octahedral sites is negligibly small and thus all magnetic moments have random orientation.

#### Mixed ferrites

The ferrites known as Ferroxcube are for the greater part mixed crystals of two or more single ferrites and as such are denoted here as "mixed ferrites". The most important of these are the MnZn ferrites (Ferroxcube III) and the NiZn ferrites (Ferroxcube IV).

Examination by X-ray diffraction shows that the Zn ions in these mixed ferrites occupy tetrahedral sites, just as is the case of zinc ferrite. The Mn and Ni ions occupy octahedral sites, as is the case for Mn and Ni ferrites. The ferric ions occupy the remaining tetrahedral and octahedral sites. The distribution may be represented symbolically by the formula:



<sup>9)</sup> From the values given in column 6 one can find the saturation polarization in  $\text{Wb/m}^2$  by multiplying those values by 7.0 times the apparent density in  $\text{g/cm}^3$  (table III, column 2) divided by the molecular weight in grammes. The saturation polarization  $J_s$  in  $\text{Wb/m}^2$  equals the saturation magnetization  $M_s$  in A/m multiplied by  $\mu_0$ .

<sup>10)</sup> L. Néel, Ann. Physique 3, 137, 1948.

<sup>11)</sup> For a more extensive treatise in connection with these assumptions see the article quoted in note <sup>10)</sup>.



If the Zn content is small there are sufficient ferric ions in the tetrahedral sites to cause all the magnetic moments on the octahedral sites to be mutually parallel. As already seen, in that case the saturation magnetization is given by the difference of the partial magnetizations of the two lattice sites. Since, owing to the presence of (non-magnetic) Zn ions the partial magnetization of the ions in

The Curie temperature of mixed ferrites

Table II gives the Curie temperature ( $T_c$ ) of NiZn ferrites with different Zn contents. It shows that the Curie temperature decreases gradually with increasing Zn content, and such appears to be the case with all mixed Zn ferrites. It is therefore possible to produce materials with a Curie temperature as low as may be desired, in the form of

Table II. The saturation magnetization  $M_s$  in Bohr magnetons per molecule and the Curie temperature  $T_c$  for different NiZn ferrites.

Ions in tetrahedral sites	Ions in octahedral sites	$M_{s\text{theor.}} = M_{s\text{oct.}} - M_{s\text{tetr.}}$	$M_{s\text{exp.}}$	$M_{s\text{theor.}} - M_{s\text{exp.}}$	$T_c$ in °C
Fe <sub>1.0</sub>	Ni <sub>1.0</sub> Fe <sub>1.0</sub>	(2.3+5.0)−5.0=2.3	2.3	0	585
Zn <sub>0.1</sub> Fe <sub>0.9</sub>	Ni <sub>0.9</sub> Fe <sub>1.1</sub>	(2.1+5.5)−4.5=3.1	2.9	0.2	530
Zn <sub>0.3</sub> Fe <sub>0.7</sub>	Ni <sub>0.7</sub> Fe <sub>1.3</sub>	(1.7+6.5)−3.5=4.7	4.2	0.5	435
Zn <sub>0.5</sub> Fe <sub>0.5</sub>	Ni <sub>0.5</sub> Fe <sub>1.5</sub>	(1.1+7.5)−2.5=6.1	5.0	1.1	295
Zn <sub>0.7</sub> Fe <sub>0.3</sub>	Ni <sub>0.3</sub> Fe <sub>1.7</sub>	(0.7+8.5)−1.5=7.7	3.9	3.8	85

the tetrahedral sites will be less than that in the case of pure Ni ferrite (or Mn ferrite), the saturation magnetization of a mixed ferrite will increase with the Zn content (at least as long as the concentration of Zn ions remains small).

This has indeed been found experimentally; see table II.

Under certain circumstances the replacement of magnetic ions in a ferromagnetic material by non-magnetic ions thus increases the saturation magnetization, which at first sight seems remarkable.

The above-mentioned restriction that this increase occurs only for low Zn contents can be explained as follows <sup>12)</sup>. For large concentrations of Zn ions it will happen that, at least in some small parts of the crystal, there are so few magnetic ions in tetrahedral sites that in those parts of the crystal the tetrahedral-octahedral interaction tending to give the moments on the octahedral sites a mutually parallel orientation is no longer capable of overcoming the influences, mentioned above for zinc ferrite, tending to give the magnetic moments either anti-parallel or random orientations. As a result the saturation magnetization is reduced (see fig. 2).

The anti-parallel orientation of the moments makes the maximum saturation magnetization attainable for a ferrite comparatively small. Metallic iron has a saturation magnetization three times as large. Consequently, for applications where a high induction is desired and high frequencies do not occur, such as for power transformers, Ferroxcube is obviously less suitable.

mixed ferrites with a suitable zinc content. It will be shown that this possibility is of great practical value.

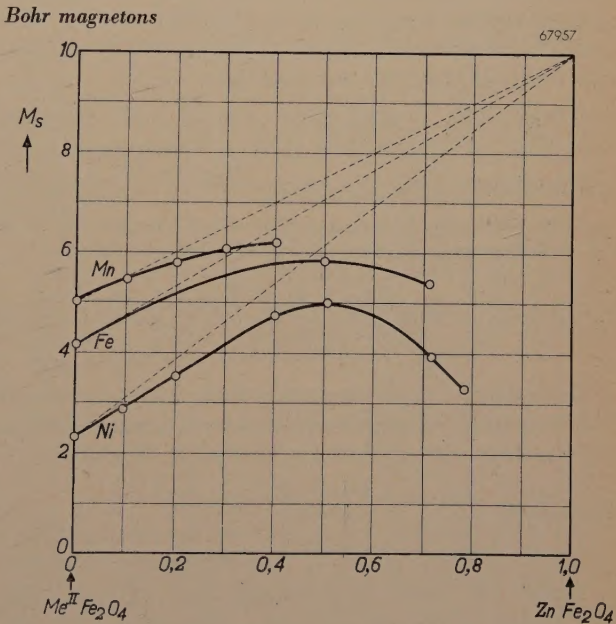


Fig. 2. The saturation magnetization of mixed ferrites, plotted in Bohr magnetons per molecule as a function of the zinc ferrite content, for different mixed ferrites. The broken lines would represent this relationship if the ions in the tetrahedral sites were always able to direct the magnetic moments of the ions in the octahedral sites. With increasing zinc content (in the tetrahedral sites) however the directing action decreases, owing to the small number of magnetic ions remaining in the tetrahedral sites. This accounts for the shape of the curves drawn, which coincide with the broken lines when the Zn content is zero but diverge from those lines as the Zn content increases.

<sup>12)</sup> E. W. Gorter, Nature 165, 798, 1950; C. R. Paris, 230, 192, 1950.



The behaviour described may be explained qualitatively in the following way.

It is known that in a simple ferromagnetic material with only one kind of lattice sites the average energy of a magnetic moment at the Curie point due to the heat movement,  $kT_c$ , is of the same order as the average energy which would be required to invert a moment when starting from a state of complete orientation. This energy is proportional to the average number of nearest neighbouring sites occupied by magnetic ions.

This picture is easily generalized for the case of ferrites where there are magnetic moments on two kinds of lattice sites, and thus magnetic moments with two kinds of surroundings. If the ratio of the number of magnetic ions on tetrahedral sites to the number of magnetic ions on octahedral sites is  $t/o$  ( $t + o = 1$ ), then the order of the quantity  $kT_c$  is given by  $t \cdot E_t + o \cdot E_o$ , where  $E_t$  and  $E_o$  are the energies which, starting from complete orientation ( $T = 0^\circ\text{K}$ ), would be required to invert respectively a moment on a tetrahedral site and a moment on an octahedral site. (Here all differences between kinds of magnetic ions and the interactions between ions in equivalent sites are ignored.)

Comparing now, for instance, pure Ni ferrite  $\text{Fe}(\text{NiFe})\text{O}_4$  with NiZn ferrite  $\text{Zn}_x\text{Fe}_{1-x}(\text{Ni}_{1-x}\text{Fe}_{1+x})\text{O}_4$ , we see that the energy required to invert a "tetrahedral moment",  $E_t$ , (to the approximation used here) will be the same in both cases, while the energy needed to invert an "octahedral moment",  $E_o'$ , will be less for the NiZn ferrite than for the Ni ferrite ( $E_o$ ), because in the mixed ferrite an octahedral moment has fewer magnetic "tetrahedral neighbours"; the relation will be  $E_o' = (1-x)E_o$ , since the average number of magnetic neighbours of an octahedral site in NiZn ferrite will be  $(1-x)$  times the number of neighbours of an octahedral site in Ni ferrite.

Finally, therefore, for the Curie temperature  $T_c$  we have approximately in the case of  $\text{Fe}(\text{NiFe})\text{O}_4$ :

$$kT_c \approx \frac{1}{3} E_t + \frac{2}{3} E_o = \frac{1}{3} (E_t + 2E_o),$$

and for  $\text{Zn}_x\text{Fe}_{1-x}(\text{Ni}_{1-x}\text{Fe}_{1+x})\text{O}_4$ :

$$\begin{aligned} kT_c &\approx \frac{1-x}{3-x} E_t + \frac{2}{3-x} E_o' = \\ &= \frac{1-x}{3-x} (E_t + 2E_o) = \frac{1-x}{1-x} \frac{1}{3} (E_t + 2E_o). \end{aligned}$$

The resulting Curie temperature  $T_c$  for NiZn ferrite for all values of  $x$  ( $0 < x < 1$ ) is lower than that for pure Ni ferrite and decreases with increasing  $x$  (increasing Zn content)<sup>13</sup>.

## Resistivity

The resistivity of  $\text{Fe}_3\text{O}_4$  (ferrous ferrite) is about a factor  $10^3$  times larger than that of iron. The resistivity of the single ferrites derived from  $\text{Fe}_3\text{O}_4$  is very much larger than even this, being a factor of about  $10^{11}$  greater than that of iron.

The relatively low value of the resistivity of  $\text{Fe}_3\text{O}_4$  can be understood by considering the crystallographic structure described above<sup>14</sup>). In this material

—which can be written as  $(\text{Fe}^{3+})_{\text{tetr.}}(\text{Fe}^{2+}\text{Fe}^{3+})_{\text{oct.}}\text{O}_4$  — ferrous ions of different valency are practically distributed at random among equivalent lattice sites, viz. among the octahedral sites. It requires apparently little energy to move an electron from a divalent ion to a trivalent one, because after this displacement of the electron the distribution of the divalent and trivalent ferric ions among the octahedral sites will again be arbitrary. This easy displacement of the electrons from divalent to trivalent ions means that the resistivity is low.

In mixed ferrites containing  $\text{Fe}^{2+}$  ions the influence of this mechanism, with corresponding reduction of the resistivity, can also be detected. The significance of this will be made clear below.

## Behaviour in weak fields

### Initial permeability

In addition to the saturation magnetization the magnetic permeability is also of great practicable importance. As a rule the highest possible permeability is desired. This permeability,  $\mu$ , depends upon the strength of the field, the magnetic history (field strength at earlier moments) and the presence of a constant polarizing field. Further,  $\mu$  is dependent upon the frequency — at least at high frequencies — and upon the temperature.

In high-frequency technique materials are mostly used in the demagnetized state and, moreover, with weak fields, so that particular attention must be paid to the initial permeability  $\mu_i$ . The conditions for which a high value can be obtained for  $\mu_i$  will now be considered.

These conditions are:

- 1) A sufficiently high value of the saturation magnetization; this quantity has already been discussed at some length.
- 2) The smallest possible amount of non-magnetic impurities and voids in the material. This point particularly needs attention in the case of ferrites because, as already mentioned, these are obtained by a sintering process, with the result that the maximum density is not reached and there is always a certain small quantity of voids.
- 3) The smallest possible magnetic anisotropy. In a certain sense magnetic anisotropy is the cause of a finite (not infinitely large) permeability; the term magnetic anisotropy is used to denote all phenomena which promote magnetization in a certain preferential direction (possibly differing from point to point in the material) or which, in other words, obstruct magnetization in the direction of the external magnetic field. There are three

<sup>13</sup>) For a more quantitative treatment see K. F. Niessen, *Physica* **17**, 1033, 1951.

<sup>14</sup>) J. H. de Boer and E. J. W. Verwey, *Proc. Phys. Soc.* **49**, extra part, 59, 1937.



factors contributing towards magnetic anisotropy: the crystal anisotropy, the stress anisotropy and the shape anisotropy.

a) Crystal anisotropy

From the point of view of energy it is often advantageous if the magnetization is oriented in a certain crystallographic direction. The energy  $E$  of each magnetic moment thus depends upon the angle  $\theta$  between its direction of orientation and the preferential direction in question. Thus a couple  $-dE/d\theta$  acts upon each elementary magnet, tending to turn it into the preferential direction. It is known that in general this crystal anisotropy, as it is called, decreases with rising temperature, and considerably below the Curie point it may often decrease to a very small value. For our considerations it is not so much the absolute temperature  $T$  that is of importance but rather the (reduced) temperature relative to the Curie point,  $T^* = T/T_c$ . For a given absolute temperature, the relative temperature  $T^* = T/T_c$ , which determines the value of the anisotropy, becomes higher as  $T_c$  is lowered. As pointed out by Snoek, it is desirable to make the Curie temperature as low as is compatible with the purpose for which the material is to be used <sup>15)</sup>. (The temperatures which occur in the practical application must obviously always be kept below the Curie point.)

By employing the method already mentioned for reducing the Curie point (preparation of a mixed Zn ferrite) it is therefore possible to satisfy

one of the conditions for the highest possible initial permeability  $\mu_i$ . (See also *table III*, columns 4 and 6.) This procedure is particularly effective in the case of Ni ferrite, since the crystal anisotropy of this material has been found to be much larger than that of Mn ferrite.

b) Stress anisotropy

Stresses (internal as well as external) in a ferromagnetic material as a rule give rise to anisotropy. The magnetic moments show a preference to be oriented parallel to the direction of the stress  $\sigma$  or in a plane perpendicular to it, according to the sign of the magnetostriction constant  $\lambda$ . The magnitude of this anisotropy is always proportional to the product  $\lambda\sigma$  <sup>16)</sup>.

During the cooling of a polycrystalline material internal stresses are always set up in a solid substance, partly through non-isotropic thermal expansion and partly through other causes. The thermal expansion in cubic crystals is isotropic, and it is for this reason that all Ferroxcube materials consist exclusively of cubic ferrites. Considering, however, the small internal stresses still remaining even in a cubic material, though it may be cooled with the utmost care, it is endeavoured to keep magnetostriction small if a high initial permeability is desired.

As is the case with crystal anisotropy, magnetostriction usually decreases as the temperature approaches the Curie temperature. With respect to magnetostriction it is therefore also desirable to make the Curie temperature as low as possible <sup>17)</sup>.

<sup>15)</sup> The saturation magnetization is also a function of  $T^*$ , decreasing with increasing  $T^*$  in all ferromagnetic materials so far known. From the fact that by raising  $T^*$  the value of  $\mu_i$  is actually increased it can be concluded that in general the favourable effect of the decrease of the crystal anisotropy is greater than the adverse effect of decrease of the saturation magnetization.

<sup>16)</sup> If the material is isotropic in respect to magnetostriction, the work required per  $\text{cm}^3$  to cause the magnetization to turn over an angle  $\varphi$  away from the direction of the tensile stress  $\sigma$  is given by  $E = \frac{3}{2} \lambda \sigma \sin^2 \varphi$ .

<sup>17)</sup> See also: J. L. Snoek, *New developments in ferromagnetic materials*, Elsevier Publishing Comp., New York — Amsterdam 1947.

**Table III.** Some properties of different kinds of Ferroxcube. The values apply to representative samples taken from the normal production of each material.

Material	Apparent density in $\text{g/cm}^3$	Saturation polarization*) at 20 °C in $10^{-4} \text{ Wb/m}^2$	Initial permeability $\mu_i/\mu_0$	$\mu_0 \frac{d\mu_i}{\mu_i^2 dT}$	Curie temp. $T_c$ in °C	$\mu''/\mu'$ at 100 kc/s	Freq. at which $\tan \delta = 0.1$ in kc/s	Saturation magnetostriction $\lambda_s \times 10^6$	Resistivity $\rho$ for direct current in $\Omega\text{m}$	Dielectric constant $\epsilon_r$ at low frequencies
III <sup>A</sup>	4.93	3350	1750	+ 3.7	130	0.02	300	— 1.0	1.8	} appr. $10^5$
III <sup>B</sup>	4.93	4650	1245	+ 0.5	160	0.01	460	— 0.5	1.5	
III <sup>C</sup>	4.91	4750	1280	+ 2.9	190	0.017	420	between —0.5 and 0	0.6	
III <sup>D</sup>	4.78	5100	806	+ 4.2	235	0.010	830	— 1.1	1.0	
IV <sup>A</sup>	4.90	3665	650	+ 9	140	0.013	1 500	— 4.2	} $> 4 \cdot 10^4$	} appr. $10^3$
IV <sup>B</sup>	4.55	4170	230	+13	265	0.015	5 500	— 7.5		
IV <sup>C</sup>	4.17	4030	90	+20	385	0.010	16 000	—15.5		
IV <sup>D</sup>	4.07	3550	45	+27	465	0.006	29 000	—18.5		
IV <sup>E</sup>	4.04	2460	17	+40	585	0.006	60 000	—22		
Column 1	2	3	4	5	6	7	8	9	10	11

\*) As is known, the saturation polarization for metallic iron is in the order of  $15000 \cdot 10^{-4} \text{ Wb/m}^2$ .



As a matter of fact there is yet another way to reduce magnetostriction to a negligible value. For all ferrites except ferrous ferrite the magnetostriction is found to be negative.  $\text{Fe}_3\text{O}_4$  has a large positive magnetostriction. Therefore by preparing a mixed ferrite with only a small quantity of  $\text{Fe}_3\text{O}_4$  (this means the introduction of divalent iron ions), using ferrites already having a small (negative) magnetostriction, such as  $\text{Mn}$  ferrite or  $\text{MnZn}$  ferrite, the magnetostriction can be reduced to a negligible value. When applying this method of increasing the initial permeability it must be borne in mind, however, that at the same time also the resistivity is decreased (and with this the eddy-current losses); this therefore limits the amount of  $\text{Fe}_3\text{O}_4$  that can be introduced in the mixed crystal.

The ferrites denoted by the name of Ferroxcube III are all  $\text{MnZn}$  ferrites with practically zero magnetostriction. As a result, however, their resistivity is rather low, lying for the different kinds of Ferroxcube III between 0.5 and 2  $\Omega\text{m}$  (see table III, columns 9 and 10).

### c) Shape anisotropy

A non-spherical body, even when crystal and stress anisotropy are absent, always has a preferential direction of magnetization, viz. the direction for which the demagnetizing field is the minimum (i.e. the direction of its greatest dimension). A non-spherical void in a ferromagnetic medium is equivalent to a non-spherical magnetic body in non-ferromagnetic surroundings, in the sense that a preferential direction exists also for the apparent magnetization of that void in a ferromagnetic medium, whose magnetization is opposed to that of the medium. This means that the magnetization of the medium in which the void is situated will preferentially be parallel to the direction of the longest dimension of the void. Therefore, in preparing the ferrite care must be taken that the inevitable voids are as far as possible spherical and as few as possible in number.

### The temperature-dependence of permeability

From what has been said about the crystal anisotropy and magnetostriction it follows that in general the initial permeability  $\mu_i$  increases with rising temperature and reaches a maximum in the neighbourhood of the Curie temperature. The temperature coefficient of the initial permeability is therefore as a rule positive (see fig. 3 and table III, column 5). If, in addition to a very weak alternating field, also a constant polarizing field  $H_p$  is applied, then the permeability corresponding to the alter-

nating field is the reversible permeability  $\mu_{\text{rev}}$ . The temperature coefficient for this permeability is as a rule smaller than that for the initial permeability. For certain values of the polarizing field that coefficient may even assume negative values.

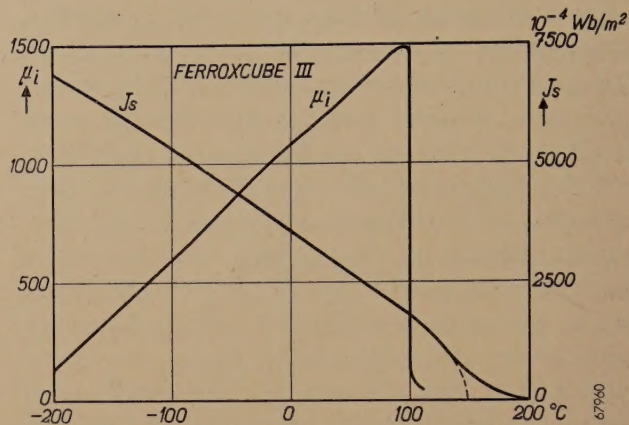


Fig. 3. The saturation polarization  $J_s$  and initial permeability  $\mu_i$  of Ferroxcube III as functions of temperature.

This behaviour is easily understood. The polarization  $J$  of the material as a function of  $H$  is given for two different temperatures by the two magnetization curves in fig. 4. When the temperature is raised, the normal  $J$ - $\mu_0 H$  curve changes into the curve given by the broken line. The general trend of this latter curve is at once clear when it is borne in mind that with increasing temperature the saturation magnetization decreases and the initial permeability increases. The steeper the slope of the magnetization curve at the point with abscisse  $H_p$ , the larger the permeability  $\mu_{\text{rev}}$  will be.

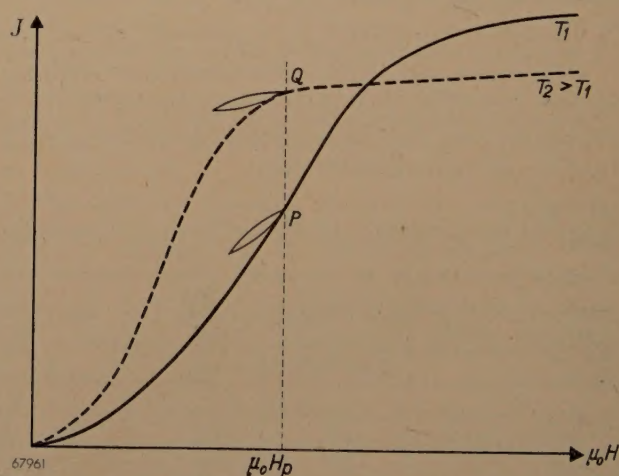


Fig. 4. The relation between the polarization  $J$  and the field  $\mu_0 H$  for different temperatures. The points  $P$  and  $Q$  of the magnetization curves give the values of the polarization in the field  $H_p$  at two different temperatures  $T_1$  and  $T_2 > T_1$ . The reversible permeability  $\mu_{\text{rev}}$  for very small alternating fields, superimposed on  $H_p$ , increases with the slope of the magnetization curve at the point with abscisse  $H_p$ . It is seen that  $\mu_{\text{rev}}$  is greater at  $P$  than at  $Q$ , the temperature coefficient of  $\mu_{\text{rev}}$  being negative there, while in the case of a polarizing field  $H_p = 0$  it is positive.



Fig. 4 shows quite clearly that for the chosen value of  $H_p$  the quantity  $\mu_{rev}$  is smaller for the high temperature than for the low one. Thus for this value of  $H_p$  the temperature coefficient of  $\mu_{rev}$  is negative.

From the foregoing it can be seen that by applying a polarizing field of suitable magnitude the temperature coefficient of the permeability can be adjusted within wide limits, making it either positive or negative and even zero.

Losses at low values of the induction

In the introduction it was already pointed out that in Ferroxcube materials the eddy-current losses are generally negligible, owing to the high resistivity of these materials. Therefore only the hysteresis and residual losses have to be considered. It appears that for low values of the induction the hysteresis losses (which can be determined, for instance, from the hysteresis curve) usually form only a small proportion of the total losses measured. The residual losses, which in this case are therefore responsible for the greater part of the total losses, can be dealt with by regarding the permeability  $\mu$  as a complex quantity:  $\mu = \mu' - j\mu''$ , thus giving expression to the fact that the induction  $B$  comprises two components, one in phase with the field applied (and determined by  $\mu'$ ) and one  $90^\circ$  in phase behind the field (determined by  $\mu''$ ). The resulting induction  $B$  is therefore a certain (small) angle behind the field applied; the phase angle (loss angle) is given by  $\tan \delta = \mu''/\mu'$ .

The loss factor accompanying the occurrence of a complex permeability is given by:

$$\frac{\Delta R}{\mu_r' f L} = \frac{2\pi}{\mu_r'} \cdot \frac{1}{Q} = 2\pi \frac{\tan \delta}{\mu_r'}$$

From this it follows directly that the behaviour of  $\mu''$  is just as much a matter of interest as the behaviour of  $\mu'$ .

If the ferrite has been prepared with the necessary care, so that the presence of voids and of foreign phases is avoided as far as possible and the internal stresses are small, then it appears that the quantity  $\tan \delta$  at low frequencies varies but little for the various kinds of Ferroxcube and is always in the order of 0.01 (see table III column 7);  $\mu'$  on the other hand may assume widely different values. For use at low frequencies a ferrite with the highest possible  $\mu'$  is therefore the most advantageous.

At higher frequencies complications arise owing to the fact that both  $\mu'$  and  $\mu''$  are frequency-dependent. This dependence upon frequency may roughly be described as follows (see figs 5 and 6).

Up to a certain critical frequency the real part  $\mu'$  of  $\mu$  is practically independent of the frequency, but above that it shows a definite decrease with increasing frequency. In the critical frequency range  $\mu''$  reaches a maximum value.

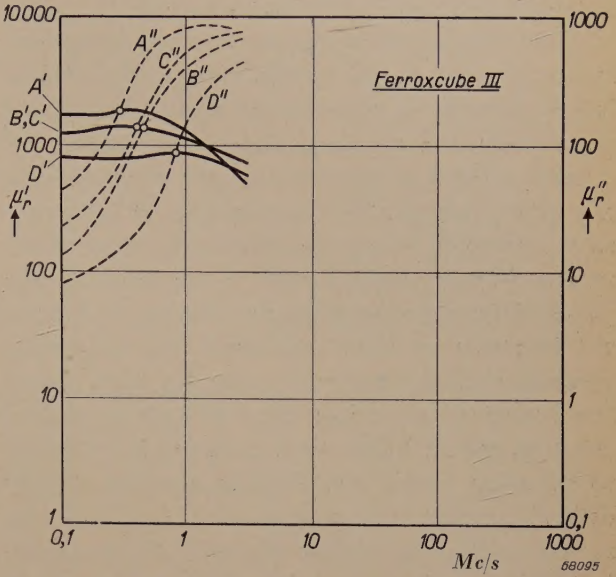


Fig. 5. The real and the imaginary parts of initial permeability,  $\mu_r'$  and  $\mu_r''$ , as functions of the frequency, for different kinds of Ferroxcube III.

A relationship has been found to exist between the critical frequency and the low-frequency value of  $\mu'$ : the smaller the value of  $\mu'$ , the higher is the critical frequency. This relationship, first found and interpreted by Snoek <sup>18)</sup>, is graphically illustrated in figs 5 and 6.

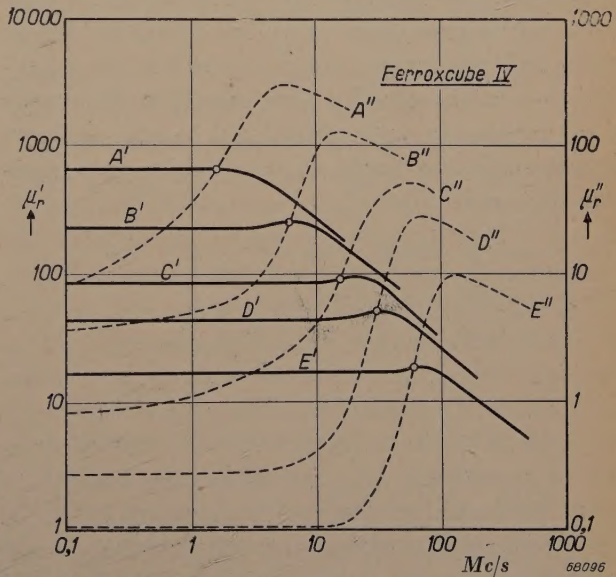


Fig. 6. The same as in fig. 5 but for different kinds of Ferroxcube IV.

<sup>18)</sup> J. L. Snoek, Nature **160**, 90, 1947; Physica **14**, 207, 1948.



This dependence of  $\mu'$  and  $\mu''$  upon frequency in the range between 1 and 200 Mc/s is probably due to the ferromagnetic resonance absorption, a phenomenon directly related to the fact that the magnetic moments in a ferromagnetic material are, as it were, small spinning tops with a certain rotational impulse.

When such a top is subjected to a couple tending to direct it into a certain state of equilibrium it will describe a precessional movement around the equilibrium position; the corresponding frequency will be proportional to the magnitude of the acting couple. The phenomenon of ferromagnetic resonance then arises when a magnetic alternating field is applied with a component perpendicular to the equilibrium position, and when the frequency of that field equals the precession frequency of the magnetic spinning tops. When the acting couple arises from the presence of a constant external field then each top is subjected to the same couple and there is a rather sharply defined resonance frequency. The fact that the resonance frequency is not sharp is due to damping. This damping, which is caused by the mutual interaction of the magnetic moments or of their interaction with the crystal lattice, also gives rise to the losses occurring with the resonance phenomenon (the resonance absorption).

The occurrence of a directional couple in a ferrite in the demagnetized state is to be ascribed to the magnetic anisotropy, which may have widely differing values at different places in the material. As a result the spinning tops have different precession frequencies, and that is why with ferrites absorption is found to take place in a wide frequency range. Thus it is understood how a high initial permeability — which means a low magnetic anisotropy and therefore a weak directional couple — is accompanied by a low resonance frequency, as previously remarked.

Behaviour in strong fields

Permeability at high field strengths

It has been mentioned that for most applications at high frequencies only weak fields are of interest, and on that account the initial permeability was the quantity with which we were primarily concerned. However, not all applications are confined to weak fields, and moreover it is of interest also from the physical point of view to know something about the magnetization processes taking place in the presence of stronger fields, of different frequencies.

In *figs 7 and 8* the magnetization curves of Ferroxcube III<sup>B</sup> and IV<sup>C</sup> are represented for different

frequencies. These curves reveal the remarkable fact that in the case of Ferroxcube III<sup>B</sup> the permeability for high field strengths is frequency-dependent between 50 and 500 kc/s, whereas in

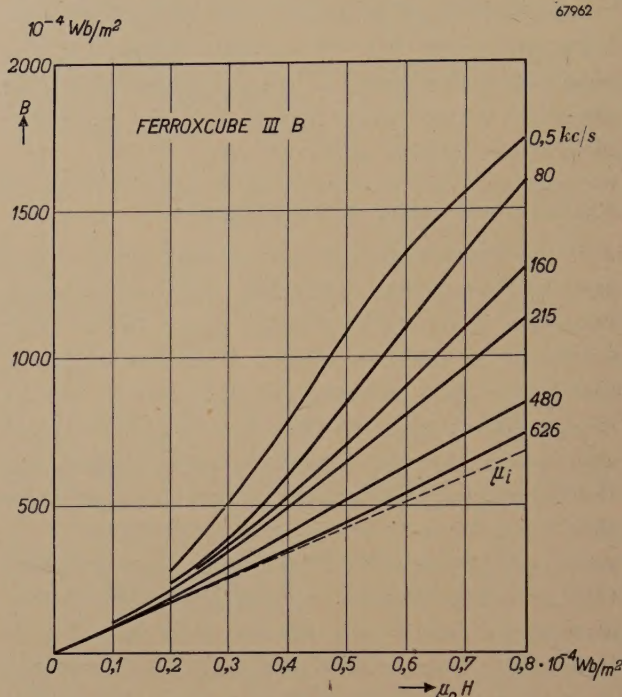


Fig. 7. Magnetization curves of Ferroxcube III<sup>B</sup> for different frequencies.

the case of Ferroxcube IV<sup>C</sup> it is independent of frequency up to at least 1 Mc/s. With increasing frequency the magnetization curves for Ferroxcube III<sup>B</sup> approach more and more a straight

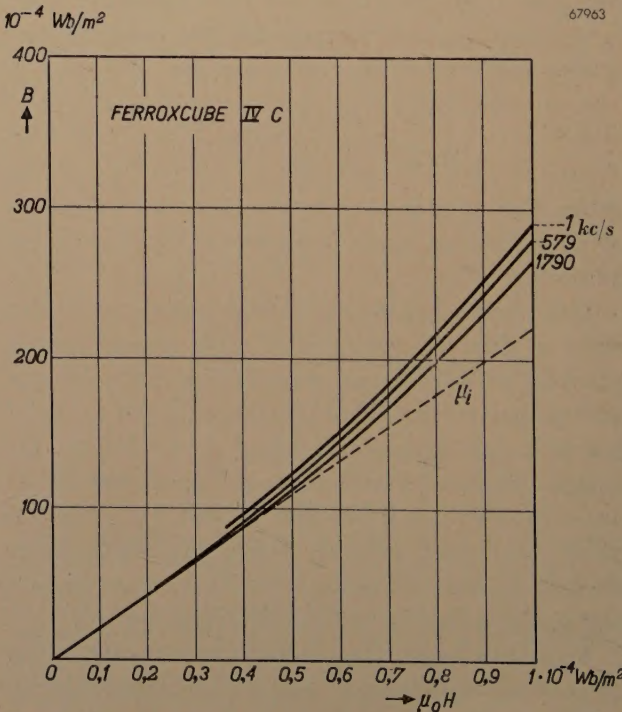


Fig. 8. Magnetization curves of Ferroxcube IV<sup>C</sup> for different frequencies.



line, with a slope approximately equal to the initial permeability. The latter quantity, as already seen from fig. 6, is for both materials independent of frequency up to the ferromagnetic resonance frequency.

It would lead us too far afield to go into this behaviour in every detail<sup>19</sup>), but considering the great importance of a good understanding of the magnetization process in ferrites it is necessary to note the most important conclusions to be drawn from the curves given in figures 7 and 8.

It is known that the character of the magnetization curve (the  $J-\mu_0 H$  curve) in ferromagnetic materials is directly dependent upon the fact that such a material in the demagnetized state is divided into Weiss domains. Within such a domain the magnetization has always the saturation value and it is orientated in a certain preferential direction (see note <sup>5</sup>)). As a rule this preferential direction is not the same for different domains. The domains are mutually separated by a boundary layer (Bloch wall) in which the magnetization changes direction, gradually turning away from the preferential direction in one domain to that in another.

For the metallic ferromagnetic materials hitherto commonly employed the transition from the demagnetized state to a state of total magnetization differing from zero (the magnetization process) is imagined to be as follows.

In the case of very weak fields magnetization is brought about by reversible displacements of the Bloch walls, the domains whose magnetization is orientated roughly in the direction of the field growing at the expense of the domains in which the direction of magnetization is against the field direction. In the presence of stronger fields these reversible wall displacements change into irreversible ones. Finally, in the case of even stronger fields, when the magnetization through wall displacements cannot increase any more, the magnetization in the domains themselves turns in the direction of the field.

The picture that we have of the magnetization process in ferrites differs considerably from that given above. The magnetization in very weak fields is believed to take place through rotation of the magnetization in the Weiss domains, and not through reversible wall displacements. In ferrites wall displacements occur only in the presence of stronger fields.

This picture of the magnetization process in ferrites is based upon the curves given in figures

7 and 8 together with the fact, now practically established, that the phenomenon of ferromagnetic resonance absorption originates in the rotation of the elementary magnets within a domain, and not in a wall displacement.

From the relationship found to exist between the value of the initial permeability and the value of the ferromagnetic resonance frequency it can be concluded, almost with certainty, that the initial permeability at that frequency is determined exclusively by rotations. Figures 7 and 8 show that up to the resonant frequency the initial permeability is independent of frequency. In other words, the initial permeability is exclusively governed by rotations not only at the ferromagnetic resonance frequency itself but also at the frequencies below it.

The reason why no wall displacements take place in the presence of weak fields may be understood when considering that, as already explained, in Ferroxcube materials small voids are always present, and it appears that such inhomogeneities always fix a Bloch wall to a certain extent. Apparently in Ferroxcube materials the walls are fixed by the voids at so many points that any (reversible) displacement or bulging of the walls under the influence of a weak field is so limited as to yield no perceptible contribution to the magnetization. It is only when the fields are of sufficient strength to release the walls from the voids that the magnetization process by irreversible wall displacements is superimposed on the magnetization process by reversible rotations. The introduction of a new process contributing towards the magnetization is evident in figures 7 and 8 from the fact that with stronger fields the magnetization curve shows a deviation from the straight line.

From the fact that in the case of some ferrites these deviations from a straight line disappear at frequencies above 200 to 500 kc/s — in this case the permeability above these frequencies is almost independent of the field strength — it may be concluded that obstructive mechanisms are operative which prevent any displacement of the walls above these frequencies.

#### *Magnetic losses at high induction values*

When the induction reaches high values the contribution of hysteresis losses towards the total losses is no longer negligible. As already explained, it is not possible, however, to separate the contributions of hysteresis losses and residual losses in a manner as expressed by eq. (1). One of the reasons for this lies in the frequency-dependence of the

<sup>19</sup>) H. P. J. Wijn and J. J. Went, Phys. Rev. **82**, 269, 1951; and in more detail in Physica **17**, 976, 1951.



magnetization curve just dealt with, as a consequence of which also the shape of the hysteresis loop and the magnitude of the hysteresis losses are dependent upon the frequency.

Fortunately, when measuring the total magnetic losses it appears that a relatively simple relationship exists between the magnitude of these losses and  $B_{\max}$ . To find this relationship the total loss per cycle per  $\text{m}^3$ ,  $W_{\text{tot}}$ , has to be multiplied by  $\mu_r'$  (taken at the frequency and induction in question) and plotted against  $B_{\max}$ . When such curves are plotted for different frequencies (of course below

decrease at comparatively low frequencies and ultimately reaches quite normal values (10 to 20).

Further it is seen that in the same frequency range where  $\epsilon'$  begins to decrease the imaginary part  $\epsilon''$ , which determines the dielectric losses and at low frequencies is inversely proportional to  $\omega$ , decreases at a slower rate (the product  $\epsilon''\omega$  begins to increase).

The physical causes of these interesting properties, which as a matter of fact can be observed also in other semi-conductors, will not be dealt with in great detail. It may suffice to say here that they

can be understood qualitatively by assuming the materials not to be completely homogeneous electrically<sup>20)</sup>.

However, attention is to be drawn, briefly, to one practical consequence of these properties.

When a material is placed in an electric alternating field no difference can in fact be made between  $\epsilon''$  and the conductivity  $\sigma$ . From Maxwell's equations it follows that

$$\sigma = \epsilon_r'' \epsilon_0 \omega.$$

At high values of the product  $\epsilon''\omega$  the

resistivity  $\rho$  is low and one would therefore expect eddy-current losses to appear.

Indeed, the high value of  $\epsilon''$  for Ferroxcube III does result in extra losses, but these are not to be regarded simply as eddy-current losses.

Eddy-current losses are known to become perceptible as soon as the depth of penetration of the magnetic alternating field in the ferromagnetic material is of the same order as or less than the thickness of the object (skin effect). Assuming that  $\mu'' \ll \mu'$  and  $\epsilon' \ll \epsilon''$  the following formula may be derived for the penetration depth  $d$ :

$$d = \sqrt{\frac{2}{\omega \mu_r' \mu_0 \sigma}} = \frac{\lambda}{2\pi} \sqrt{\frac{2}{\mu_r' \epsilon_r''}}, \quad (3)$$

where  $\lambda$  is the wavelength of the electromagnetic

<sup>20)</sup> C. G. Koops, Phys. Rev. **83**, 121, 1951.

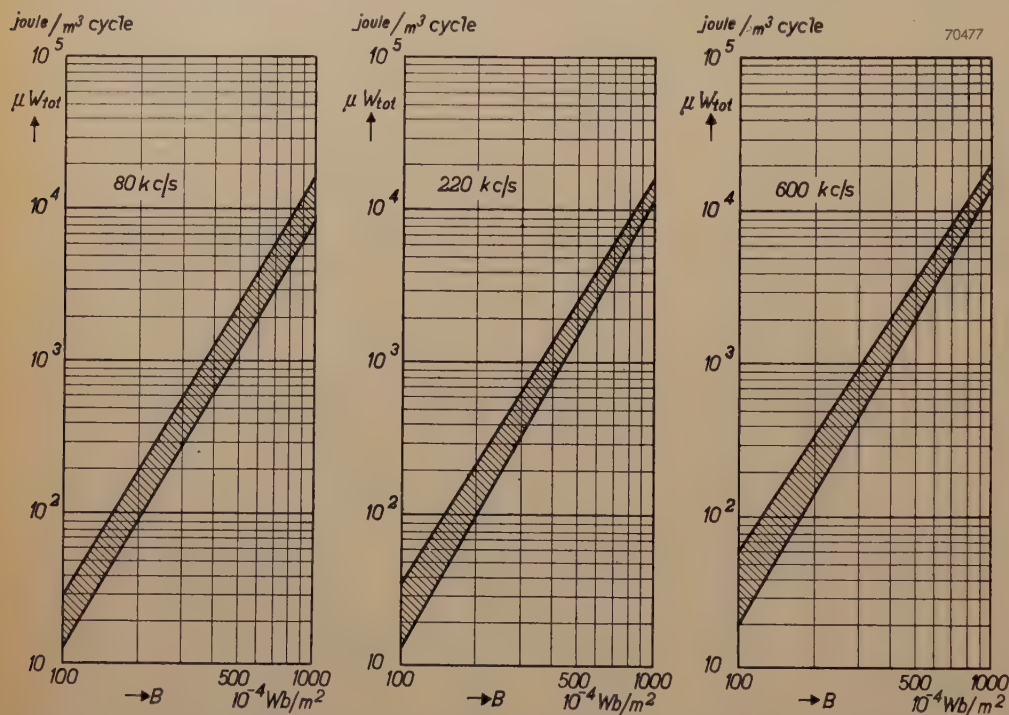


Fig. 9. Loss per cycle and per  $\text{m}^3$ ,  $W_{\text{tot}}$ , multiplied by  $\mu_r'$ , as a function of the induction  $B_{\max}$ , for different frequencies. The relationships given here apply for all kinds of Ferroxcube.

the ferromagnetic resonance frequency) it is found that one set of curves suffices for all kinds of Ferroxcube (fig. 9).

### Dielectric properties of the ferrites

In the introduction it was observed that the dielectric properties of the ferrites are rather exceptional. A glance at fig. 10 will make this clear. For the expression of the dielectric behaviour one preferably uses a complex term for the dielectric constant:  $\epsilon = \epsilon' - j\epsilon''$ , as was done for the permeability. From fig. 10, where the relative values  $\epsilon_r'$  and  $\epsilon_r''$  have been plotted as functions of the frequency ( $\epsilon = \epsilon_r \epsilon_0$ ), it appears that at low frequencies the real part  $\epsilon'$  of  $\epsilon$  for Ferroxcube III is exceptionally large (about  $10^5$ ) and decreases appreciably only at high frequencies. The value of  $\epsilon'$  is also large for Ferroxcube IV, but it begins to



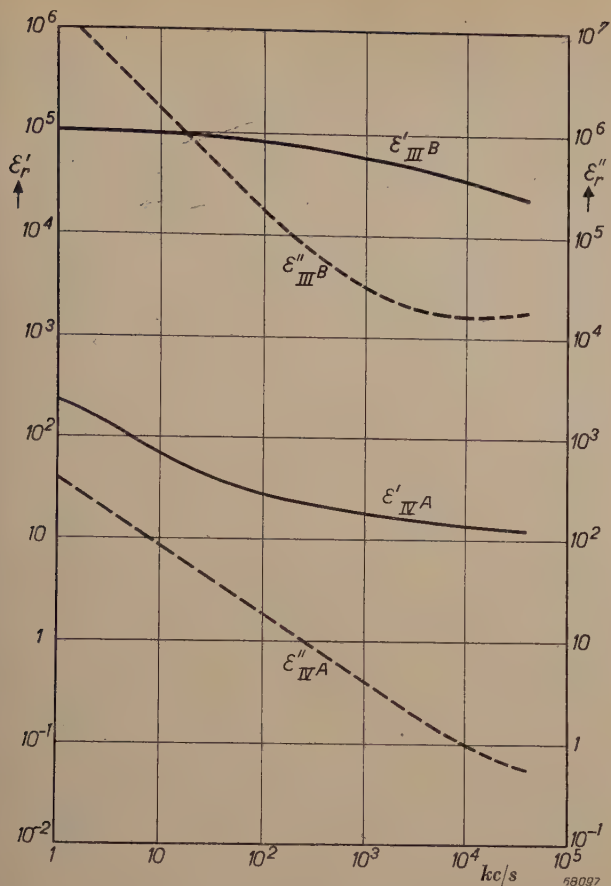


Fig. 10. The real and the imaginary parts of the dielectric constant,  $\epsilon'_r$  and  $\epsilon''_r$ , as functions of the frequency, for Ferroxcube III<sup>B</sup> and IV<sup>A</sup>.

wave in vacuo. Since it therefore depends upon the dimensions of the object at what frequency the losses begin to become noticeable, one speaks of dimensional absorption.

Taking a thickness of 1 cm, corresponding roughly to what is often used in practice, it can be calculated for Ferroxcube III, with the aid of the values of  $\mu'$  and of  $\rho$  (and thus of  $\epsilon''$ ) given in table III, that the losses in question should become perceptible at a frequency of 2.5 Mc/s. Actually, Brockman, Dowling and Steneck<sup>21</sup>) found that with a thickness of 1 cm Ferroxcube III shows additional losses even at much lower frequencies.

The explanation for this behaviour given by these investigators is that formula (3) does not apply here, because the condition  $\epsilon' \ll \epsilon''$  is not satisfied for Ferroxcube III in this frequency range. Skin effect is entirely absent. It is, however, quite possible that in this case the induction lines in the ferromagnetic material deviate from their regular

course, this being accompanied by losses. The criterion for this is that a length  $d'$ , satisfying a formula similar to that given in (3), viz:

$$d' = \frac{\lambda}{2\pi} \sqrt{\frac{2}{|\mu_r| |\epsilon_r|}},$$

is of the same order as or less than the smallest dimension of the object. Since  $d'$  is equal, except for a numerical factor, to the wavelength of the electromagnetic wave in the material, and therefore, for the occurrence of these losses, it must bear a certain relation to the dimension of the object, Brockman, Dowling and Steneck speak of dimensional resonance. For Ferroxcube III the value of  $d'$  is found to be approximately equal to 1 cm already at a frequency of 1 Mc/s.

If in a given practical case difficulties are to be feared as a consequence of this dimensional resonance, the simplest solution is to avoid the effect entirely by using Ferroxcube IV instead of Ferroxcube III. Not only is the value of  $\rho$  much larger ( $\epsilon''$  much smaller) than that for Ferroxcube III, so that eddy-current losses become perceptible only at much higher frequencies, but moreover the dielectric constant  $\epsilon'$  is already fairly small below 100 kc/s, so that within reasonable frequency limits no trouble need be feared from dimensional resonance effects.

**Summary.** Ferroxcube materials are ferromagnetic oxide materials specially developed for use at high frequencies. Their suitability for such applications lies in the fact that owing to their high resistivity eddy-current losses do not as a rule occur.

As regards the chemical composition these materials belong to the group of ferrites crystallizing with the spinel structure. The saturation magnetization of ferrites is closely related to their crystallographic structure. According to Néel the values of the saturation magnetization found experimentally can be explained by assuming that an interaction exists between magnetic moments on crystallographically non-equivalent lattice sites, which tends to give those moments an antiparallel orientation.

Although eddy-current losses do not usually occur in Ferroxcube, residual losses, given by the expression  $\tan \delta/\mu'$ , may under certain conditions be considerable. It is therefore highly important to know the behaviour of  $\mu'$  and  $\tan \delta$ , or of the real and the imaginary parts of the complex permeability  $\mu = \mu' - j\mu''$ , for all possible values of induction and of frequency. In this paper the behaviour of these quantities as a function of frequency is discussed, both for very small and for somewhat larger values of the induction. Further, the temperature dependence of the initial permeability is discussed. The behaviour of the imaginary part of the initial permeability at high frequencies is shown to bear a relationship to the ferromagnetic resonance absorption; this relationship and the behaviour of the permeability in the presence of stronger fields lead to the conclusion that the magnetization process in ferrites differs from that taking place in metallic ferromagnetic materials.

Finally attention is drawn to the remarkable dielectric properties of ferrites and the extra losses apt to arise therefrom (dimensional resonance).

<sup>21</sup>) F. G. Brockman, P. H. Dowling and W. G. Steneck, Phys. Rev. 77, 85, 1950.



# FERROXDURE, A CLASS OF NEW PERMANENT MAGNET MATERIALS

by J. J. WENT\*), G. W. RATHENAU, E. W. GORTER and G. W. van OOSTERHOUT.

621.313.12:538.246.2

*Present permanent magnet materials are in general metallic alloys mostly containing nickel or cobalt or both. Ferroxdure, the class of new permanent magnet materials developed in the Philips Research Laboratories at Eindhoven consists of oxidic ceramics which do not contain any nickel or cobalt. The interesting and typical properties of these materials and some applications of Ferroxdure are treated in the three parts of this article.*

## I. MOST IMPORTANT PROPERTIES OF FERROXDURE

### Introduction

Ferromagnetic oxides have been the object of extensive research in the Philips Laboratories for many years. The reader of this journal has had ample opportunity to get informed about one class of those materials known by the name of Ferroxcube. As was already often stated in former publications <sup>1, 2)</sup> Ferroxcube materials are characterized by possessing a high electric resistivity together with a high magnetic permeability. Because of the latter property Ferroxcube materials belong to the class of the magnetically soft materials. Ferroxcube is extremely well suited for use in high frequency inductances, high frequency transformers etc. <sup>1) 2)</sup>.

During the last two years another class of ferromagnetic oxides has been studied extensively at the Philips Research Laboratories at Eindhoven. These oxides are magnetically hard, i.e. they can be used as materials for permanent magnets. The remarkable fact about these oxides is that they do not contain any nickel or cobalt, in contradistinction to most other permanent magnet materials. This fact is of great economic importance as these two metals are expensive and at present difficult to obtain. The representatives of this class of new materials have been given the name of Ferroxdure.

### Characteristics of magnetically soft and hard materials

While magnetically soft materials are mainly characterized by their permeability and by the losses they introduce when they are placed in an alternating magnetic field, quite different

properties are characteristic for magnetically hard materials. Therefore, before entering into details we wish to give a very short survey of the quantities which are frequently used in dealing with magnetically hard materials. This is most conveniently done with the aid of figure 1a <sup>3)</sup>. In this figure the magnetization  $J$  [ $4\pi J$ ] is given as a function of the effective field  $H_i$  <sup>4)</sup>. As is well known, the magnetization of a ferromagnetic material is in general not uniquely determined by the effective field. This means e.g. that if a ferromagnetic is magnetized to its saturation magnetization, and subsequently the effective field is brought to zero in a continuous way, a certain magnetization remains, the remanent magnetization  $J_r$ . The effective field in the direction opposite to the remanent magnetization that must be applied in order to reduce the magnetization to zero is called the  $J$ -coercive field (often also the coercive force); it is indicated by the symbol  $JH_c$ . In the particular case shown in fig. 1a  $JH_c$  is of the same order of magnitude as  $J_r$  [ $4\pi J_r$ ]. A similar coercive field, the  $B$ -coercive field denoted by the symbol  $BH_c$ , can be defined, which according to a completely analogous definition is necessary to reduce the

<sup>3)</sup> For a more detailed discussion of most quantities see e.g. J. J. Went, Philips techn. Rev. **10**, 246, 1948.

<sup>4)</sup> The effective field is the difference between the external field  $H$  and the demagnetizing field  $NJ/\mu_0$  [ $N'J$ ] where  $N$  [ $N'$ ] is the factor of demagnetization in the direction of the field. Unless explicitly stated differently, in the following  $H$  will be used to denote the effective field.

Throughout this article formulae are given using the rationalized Giorgi system of electromagnetic units (see also Philips techn. Rev. **10**, 79, 1948). For the convenience of those readers who are not (yet) familiar with this system, formulae in unrationalized cgs units (Gauss system) are given between square brackets. In the figures scales for both systems of units are given.

It is to be remembered that in the Giorgi system  $B$  and  $J$  are measured in volt sec/m<sup>2</sup> or weber/m<sup>2</sup> (1 Wb/m<sup>2</sup> = = 10 000 gauss) and  $H$  in ampere/m (1000/4 $\pi$  A/m = = 79.6 A/m corresponding to 1 oersted).

In vacuum  $B = \mu_0 H$ , in which  $\mu_0 = 4\pi/10^7$  henry/m. Instead of  $H$  (in A/m) often the value of  $\mu_0 H$  (in Wb/m<sup>2</sup>) is given ( $\mu_0 H = 1$  Wb/m<sup>2</sup> corresponding to 10 000 oersted in the cgs system). In a ferromagnetic material the relation  $B = \mu H$  holds, in which  $\mu = \mu_r/\mu_0$ ;  $\mu_r$ , the relative permeability is a dimensionless number (equal to the number indicated by  $\mu$  in the cgs system).

The value of  $BH$ , which has the dimension of an energy per unit volume, is measured in (Vsec/m<sup>2</sup>)  $\times$  (A/m) = Vasec/m<sup>3</sup> = joule/m<sup>3</sup> (1 J/m<sup>3</sup> corresponding to 126 gauss  $\times$  oersted).

\*) Now with N.V. K.E.M.A., Arnhem (Netherlands).

<sup>1)</sup> J. L. Snoek, Philips techn. Rev. **3**, 353, 1946; J. L. Snoek, New developments in ferromagnetic materials, Elsevier's Publishing Comp. Amsterdam, New-York 1947; J. J. Went and E. W. Gorter, Philips techn. Rev. **13**, 1951 (No. 7). The latter article is in the following quoted as A.

<sup>2)</sup> W. Six, shortly to appear in Philips techn. Rev.



magnetic induction  $B = \mu_0 H + J$  [ $B = H + 4\pi J$ ] to zero. In fig. 1b a demagnetization curve<sup>5)</sup> is given for a ferromagnetic for which the coercive field is such that  $\mu_0 J H_c$  [ $J H_c$ ] is much smaller than the remanent magnetization  $J_r$  [ $4\pi J_r$ ]. It is seen that in contradistinction to fig. 1a, the difference between  $J H_c$  and  $B H_c$  is very small. As will be pointed out in greater detail below, the figures 1a and 1b are valid for the cases of Ferroxdure and "Ticonal" G (a well-known permanent magnet material of very high quality<sup>6)</sup>) respectively.

Neither the remanent magnetization nor the coercive field are the most adequate quantities to describe the quality of a permanent magnet material. It has been customary to characterize the usefulness of such a material by the maximum value  $(BH)_{\max}$  which the product of the magnetic induction  $B$  and the effective field  $H$  can attain on the demagne-

tization curve. The material with the greatest value of  $(BH)_{\max}$  will be able to create a given field in an air gap of a given magnetic circuit at the cost of the smallest volume of magnetic material<sup>7)</sup>. It will be clear that both a large remanent magnetization and a large coercive field are favourable for obtaining a large value of  $(BH)_{\max}$ .

### Survey of the most important properties of Ferroxdure

The name Ferroxdure denotes a class of sintered, oxidic, magnetically hard materials. In this article the discussion will be limited to three of these materials. Two of these are oxides with compositions  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{BaFe}_{18}\text{O}_{27}$  respectively. The third material is that which at the moment is available on the market under the name of Ferroxdure, and from now on when speaking simply of Ferroxdure we mean this material. It consists mainly of the oxide  $\text{BaFe}_{12}^{\text{III}}\text{O}_{19}$ . This oxide has a non-cubic, viz. hexagonal, crystal structure and has *one* axis of easy magnetization parallel to the hexagonal axis (i.e. the crystal anisotropy is uniaxial).

The uniaxial character is essential for a large coercive force in Ferroxdure, just as it was essential for the Ferroxcube materials to be composed of cubic ferrites for obtaining a low coercive force (high permeability).

The saturation magnetization of Ferroxdure is rather low compared e.g. with that of "Ticonal" G: the values at room temperature are about  $0.42 \text{ Wb/m}^2$  [4200 gauss] and  $1.41 \text{ Wb/m}^2$  [14100 gauss] respectively.

In a magnetically hard material consisting of crystals with one axis of preferred magnetization oriented at random like Ferroxdure, the remanent magnetization can in general be shown to be half of the saturation magnetization (cf. e.g. the article quoted in footnote<sup>3)</sup>). Thus the value of the remanent induction of Ferroxdure at room temperature is rather low compared with that of "Ticonal" G, namely  $0.20\text{--}0.21 \text{ Wb/m}^2$  [2000–2100 gauss] and  $1.34 \text{ Wb/m}^2$  [13400 gauss], respectively. The coercive force  $J H_c$ , however, is extremely high, namely  $\mu_0 J H_c = 0.2\text{--}0.32 \text{ Wb/m}^2$  [ $J H_c = 2000\text{--}3200 \text{ Oe}$ ], as compared with  $\mu_0 J H_c = 0.06 \text{ Wb/m}^2$  [ $J H_c = 600 \text{ Oe}$ ] for "Ticonal" G.

In fig. 1a and 1b the demagnetization curves for these two materials are given. The high coercive force of Ferroxdure combined with the rather low remanent induction causes the large difference which is found between  $J H_c$  and  $B H_c$ . The value

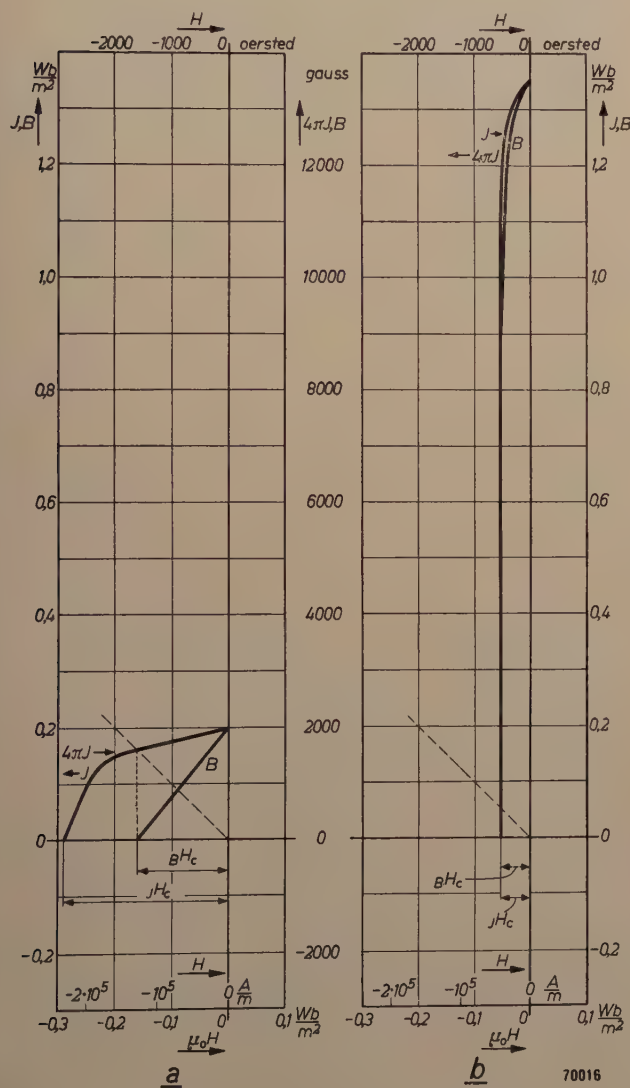


Fig. 1. Demagnetization curves for Ferroxdure (a) and "Ticonal" G (b). In a,  $J_r$  [ $4\pi J_r$ ] and  $J H_c$  are of the same order of magnitude and thus a large difference between  $J H_c$  and  $B H_c$  exists. This is not the case in b.

<sup>5)</sup> By the demagnetization curve we mean that part of the complete magnetization curve which is lying in the upper quadrant on the left.

<sup>6)</sup> See e.g. B. Jonas and H. J. Meerkamp van Embden, Philips techn. Rev. 6, 8, 1941.

<sup>7)</sup> See e.g. A. Th. van Urk, Philips techn. Rev. 5, 29, 1940. As will be pointed out later, this statement is not so strictly true as is suggested here.



of  $(BH)_{\max}$  for Ferroxdure, of about  $6800 \text{ J/m}^3$  [ $0.85 \times 10^6$  gauss oersted] is about 6 times lower than the  $(BH)_{\max}$  value for Ticonal G, which is up to  $45\,800 \text{ J/m}^3$  [ $5.7 \times 10^6$  gauss Oe]. This does not mean, however, as will be pointed out below, that the volume of magnetic material needed to create a certain field strength in an air gap of given volume is 6 times as large as that needed when using "Ticonal" G. Notwithstanding the larger volume of Ferroxdure needed, this material often will offer an economic advantage because it does not contain critical raw materials. Besides the economic advantage of Ferroxdure this material offers new technical possibilities. Its very high electric resistivity allows it to be used in high frequency applications as e.g. in Ferroxcube core transformers that need premagnetization, as deflection magnets for radar tubes or for the adjustment of the temperature coefficient of the permeability of a Ferroxcube core (cf. <sup>2</sup>). Its extremely high coercive force and the resultant strong resistance to demagnetization allow a novel approach to the design of magnetic circuits, which will be discussed in a subsequent paper to be published in this journal. Besides the above applications the following ones should be mentioned specifically: Loudspeaker circuits (see *fig. 2*), Magnets for fixing one object to another, Magnets for oil filters,



Fig. 2. Two Ferroxdure magnets as used in loudspeaker circuits magnetized in the direction of the axis. Note the disc-shaped form of the magnets which is most suitable for a material with high coercive force and relatively low remanence. The upper magnet is lifted by the field of the lower one. The external diameter of the rings is 8 cm.

Magnets for focussing electron beams,  
Electric generators and motors (see also *fig. 3*),  
Magneto-mechanic couplings.

The physical background of the various properties of Ferroxdure will be discussed in greater



Fig. 3. Rod-shaped Ferroxdure magnets which have been magnetized normal to a vertical face in such a way that on this face alternately north and south poles are formed. The ten poles on the specimen at the left and the five poles on the specimen in the centre are made visible by iron powder. Due to the low value of the permeability and the high value of the coercive force Ferroxdure is specially suited for producing strong alternating poles at a small distance from each other without the necessity of using a large extension of the specimen parallel to the direction of the magnetization.



detail in part II of this article. In order not to complicate the treatment more than necessary we shall discuss the physical properties of the main component of Ferroxdure only and of the other oxide already mentioned above, with composition  $\text{BaFe}_2^{\text{II}}\text{Fe}_{16}^{\text{III}}\text{O}_{27}$ , the crystal structure and physical properties of which are very similar to those of  $\text{BaFe}_{12}\text{O}_{19}$ . By considering also this second oxide various measurements and theoretical conclusions obtain additional confirmation.

In the first section of part II the magnetic anisotropy will be treated and it will be shown that the most important part is the (magnetic) crystal anisotropy, which is extremely high. This

large anisotropy in combination with the relatively small remanent magnetization accounts for the very high coercive force of Ferroxdure which will be discussed next. At the end of part II the following points will be discussed consecutively: the remanent induction, the demagnetization curve and the value of  $(BH)_{\text{max}}$ , and finally the electric resistivity.

In part III of this article the crystal structure of the two oxides  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{BaFe}_{18}\text{O}_{27}$  will be discussed in greater detail. It will be seen that a close relation exists between the crystal structure and the value of the saturation magnetization of these two oxides.

## II. PHYSICAL BACKGROUND OF SOME PROPERTIES OF FERROXDURE

### Magnetic anisotropy

It was already mentioned in the introduction that the magnetic anisotropy, i.e. the existence of directions of easy or preferred magnetization, is of the greatest importance for the value of the coercive field. Three different factors contribute towards facilitating magnetization in certain preferential directions: the (magnetic) crystal anisotropy, the stress anisotropy and the shape anisotropy. As will be shown in greater detail below, in the oxides treated in this paper the crystal anisotropy is large and can easily be measured. As regards the stress anisotropy: in A (cf. I, footnote <sup>1</sup>) it was shown that within a small region of the material it is proportional to the product of the linear magnetostriction constant in the direction of stress and the internal or external stress. In a sintered aggregate of non-cubic crystals large internal stresses may be expected due to an anisotropic coefficient of thermal expansion. The magnetostriction constant of Ferroxdure is not zero. Since, however, we have reason to believe that it will not greatly exceed  $10^{-5}$ , and since it is very difficult to make a quantitative estimate of the contribution of the stress anisotropy (which in fact might be appreciable) to the total anisotropy, we will tentatively leave out the stress anisotropy from our further discussion: it will be seen below that, indeed, all relevant phenomena can be explained satisfactorily by taking into account the magnetic crystal anisotropy only.

The shape anisotropy can easily be shown to be small compared with the crystal anisotropy because of the low value of the saturation magnetization.

### The crystal anisotropy

For both hexagonal oxides mentioned above, the crystal anisotropy was measured on single crystals. It was found in both cases that the hexagonal axis is the direction of easy magnetization. The so-called magnetocrystalline energy density, which describes the tendency for a preferential orientation, can be written as

$$E_c = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots \quad (1)$$

$E_c$  is the energy (per  $\text{m}^3$  [ $\text{cm}^3$ ]) necessary to turn the magnetization from the easy direction ( $\theta = 0$ ) over an angle  $\theta$ . The quantities  $K_1$ ,  $K_2$  are constants, the so-called anisotropy constants. For our purposes it is sufficient to take into account the first term of the series only, so that we have one anisotropy constant  $K_1$ , for which we shall write  $K$ . Thus formula (1) reads:

$$E_c = K \sin^2 \theta \quad (2)$$

The measurements of the anisotropy constants for the two oxides were performed as follows.

In the case of  $\text{BaFe}_{18}\text{O}_{27}$  single crystals were obtained from the melt, by H. P. J. Wijn and Y. Haven of this laboratory, that were large enough to allow the measurement of the magnetization curves in the direction of the hexagonal axis and along different directions perpendicular to it <sup>1</sup>). The hexagonal axis appeared to be the only direction of preferred magnetization, as no anisotropy within the basal plane could be detected at room temperature.

<sup>1</sup>) G. W. Rathenau and J. L. Snoek, Philips Res. Rep. 1, 239, 1945-'46.



The field strengths used were not large enough to saturate the crystal along the difficult direction. The crystal anisotropy was calculated by extrapolating the magnetization in the difficult direction to higher field strengths and measuring the area between the magnetization curves in the easy and difficult directions, this area being the work necessary to turn the saturation magnetization from the easy to the difficult direction of magnetization.

For  $\text{BaFe}_{12}\text{O}_{19}$  no single crystals were available with dimensions large enough to allow the measurement of the magnetization curves to be performed in exactly the same way. The following procedure was employed. As the basal plane is well developed for these oxides, small crystals obtained from polycrystalline material could easily be fixed on a glass plate in such a way that the hexagonal axes were perpendicular to the plate, as was confirmed by X-ray diffraction. From the results of the measurements performed on these specimens (fig. 1) the anisotropy constant could be calculated<sup>2)</sup>. In fig. 2 the values of  $K$  for the two oxides are plotted against temperature. In table I the values of  $K$  at room temperature for  $\text{BaFe}_{12}\text{O}_{19}$  are compared with those for some well-known ferromagnetics.

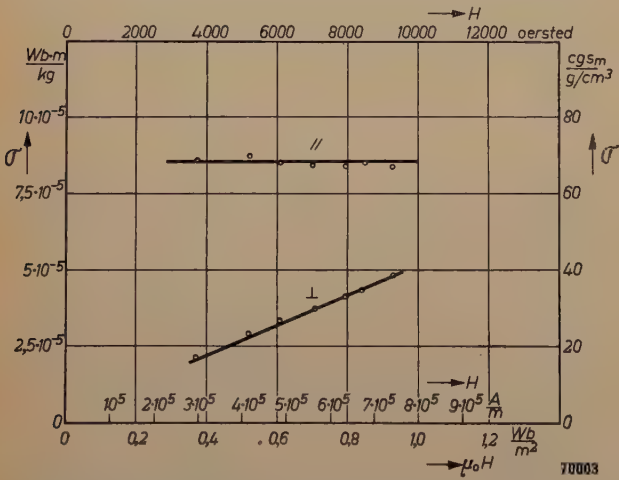


Fig. 1. Magnetic moment per unit mass  $\sigma$  as a function of a magnetizing field  $H$  at room temperature for a single crystal of  $\text{BaFe}_{12}\text{O}_{19}$ . Curve indicated by  $\parallel$ :  $H$  is parallel to the easy axis. Curve indicated by  $\perp$ :  $H$  is perpendicular to the easy axis.

Table I. The value of  $K$  at room temperature for different materials<sup>3)</sup>.

Material	$K$	
	$\text{J/m}^3$	$[\text{erg/cm}^3]$
$\text{BaFe}_{12}\text{O}_{19}$	$3 \times 10^5$	$[3 \times 10^6]$
Fe	$0.15 \times 10^5$	$[0.15 \times 10^6]$
Co	$4 \times 10^5$	$[4 \times 10^6]$

<sup>2)</sup> It was assumed that the anisotropy within the basal plane may be neglected as in  $\text{BaFe}_{18}\text{O}_{27}$ , which seems a reasonable assumption, considering the very close resemblance of the crystal structures and the experience with other hexagonal crystals, such as cobalt.

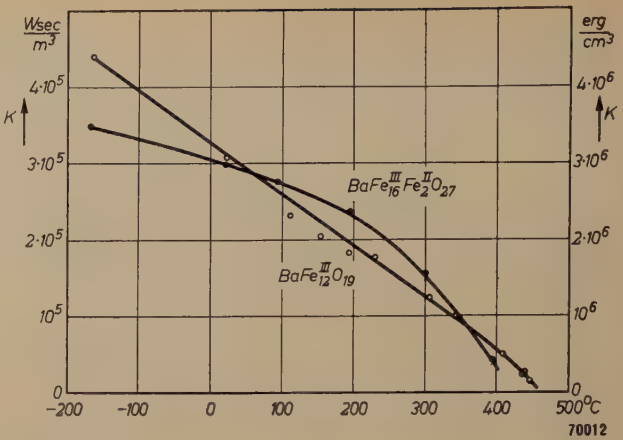


Fig. 2. Anisotropy constant  $K$  as a function of temperature.

Another method of measurement is to allow a crystal to perform torsional oscillations in a strong magnetic field in such a way that the axis of preferred orientation oscillates in a plane containing the direction of the magnetic field. By varying the field and extrapolating to fields of infinite strength the anisotropy constant  $K$  as well as the saturation magnetization can be calculated from the period of the oscillations. The results are in approximate agreement with those given in fig. 2<sup>4)</sup>.

Coercive force

There are many factors which determine in a complicated way the coercive force in the general case of a massive ferromagnetic. As Ferroxdure is a sintered material consisting of more or less small crystals with an extremely high crystal anisotropy, which have random orientation, a somewhat simpler situation may be expected<sup>5)</sup>. In order to simplify the argument we shall start with rather crude assumptions about the demagnetization process and estimate on this basis the coercive force. After comparison with experiment we shall correct our model so as to obtain better agreement with reality. It will be seen that the value of the coercive force obtained with the aid of the first assumptions gives a limit above which the coercive force can in no way be raised.

Consider a ferromagnetic single crystal saturated in its easy direction. We now assume that changes in magnetization occur only by rotation of the magnetization from the easy direction, and ask how strong a field in the direction opposite to the

<sup>3)</sup> For iron, which has cubic magnetic anisotropy, equations (1) and (2) cannot be applied. The quantity  $K$  given for iron in table I refers to the difference in magnetic energy in the  $[100]$  and  $[111]$  directions respectively.  
<sup>4)</sup> These measurements were carried out by J. Smit of this laboratory.  
<sup>5)</sup> It should be noted that a sample of the material as a whole is isotropic and that only the small crystals of which the sample is composed are anisotropic.



magnetization must be to turn the magnetization over an angle of  $180^\circ$ . If the magnetization is turned over an angle  $\Theta$  from the easy direction, the total energy density is:

$$E_t = K \sin^2 \Theta - H J_s \cos \Theta.$$

The equilibrium angle  $\Theta_e$  for a given field  $H$  is found by making  $E_t$  minimum with respect to  $\Theta$ :

$$\begin{aligned} \partial E_t / \partial \Theta &= 0; \\ 2K \sin \Theta \cos \Theta + H J_s \sin \Theta &= 0, \end{aligned}$$

This equation has two solutions. Only the first one, being  $\sin \Theta_e = 0$ , corresponds to a stable equilibrium. The other one,

$$\cos \Theta_e = -H J_s / 2K,$$

describes an unstable equilibrium. From this equation it can be seen that the absolute value of the field strength necessary to turn the magnetization from the first stable position  $\Theta_e = 0$  over a very small angle  $\Theta$  (so that  $\cos \Theta \approx 1$ ) is  $2K/J_s$ . The field strength decreases with increasing angle of deviation. Thus on applying a field  $2K/J_s$  the magnetization jumps discontinuously in the direction of the field. The field strength  $H = 2K/J_s$  is called the "turn-over" field strength.

In order to find the relation between this turn-over field strength and the coercive force of an actual sample of  $\text{BaFe}_{12}\text{O}_{19}$ , to which oxide we shall limit our discussion, the fact should be taken into account that such a sample is composed of many particles, the easy axes of which are oriented at random.

It can be shown that in this case the coercive force should lie at about  $K/J_s$ . In *fig. 3* the

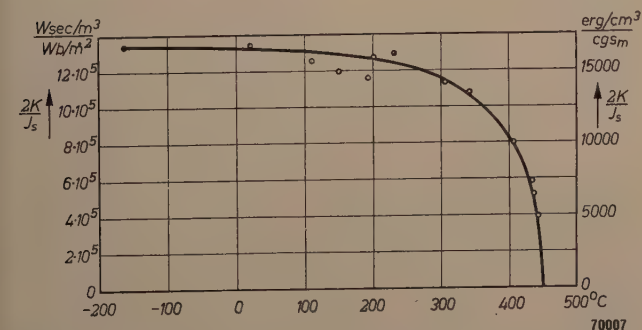


Fig. 3. The quantity  $2K/J_s$  for  $\text{BaFe}_{12}\text{O}_{19}$ , as a function of temperature.

quantity  $2K/J_s$  is plotted against temperature for  $\text{BaFe}_{12}\text{O}_{19}$ . It is seen that up to a temperature of  $250^\circ\text{C}$  the coercive force estimated on the assumption that only rotational processes occur lies near  $\mu_0 H = 0.75 \text{ Wb/m}^2$  [ $H = 7500 \text{ Oe}$ ]. The experimental value of the coercive force, though

very high, is appreciably below this value, so that our model must be modified as being too simple.

The reason for the failure of our calculation is that we did not take into account the formation and the movement of Bloch walls. The stability of a Bloch wall within a ferromagnetic particle with one direction of preferential magnetization depends on several factors<sup>6)</sup>. Let us assume that the particle has been magnetized to saturation. Its poles will create a demagnetizing field. By the formation of a wall the demagnetization energy can be diminished by an amount that is the product of a demagnetization factor, which depends on the shape of the particle, the square of the intensity of magnetization and the volume of the particle. If also an external field is applied in the direction opposite to the direction of previous magnetization the formation of the wall will reduce the energy further by an amount which is proportional to the intensity of magnetization, to the field strength and to the volume of the particle. The energy which has to be furnished in order to create the wall is determined by the "effective exchange" energy ( $J_s^2/J_0^2$ ) $kT_c$ , (where  $T_c$  is the Curie temperature)  $k$  is Boltzmann's constant and  $J_0$  the saturation magnetization at zero absolute temperature), which tends to keep the magnetic moments aligned parallel within the wall<sup>7)</sup> and by the energy of crystalline anisotropy which tends to keep the magnetic moments within the wall away from the directions of difficult magnetization. Furthermore it is proportional to the area of the wall.

In order to show that in isolated particles of  $\text{BaFe}_{12}\text{O}_{19}$  in the absence of an external field wall formation will occur only at relatively large crystal sizes, the critical diameter for wall formation at room temperature is given in *table II*, together with the maximum turn-over field strength  $2K/J_s$ , for the same materials which have been compared

Table II. The critical diameter  $d_0$  for wall formation in isolated spheres and the turn-over field strength  $2K/J_s$ .

Material	$d_0$ microns	$2\mu_0 K/J_s$ in $\text{Wb/m}^2$	$[2K/J_s]$ [oersted]
$\text{BaFe}_{12}\text{O}_{19}$	1.3	1.66	[16600]
Fe	0.028	0.018	[ 180]
Co	0.24	0.56	[ 5600]

<sup>6)</sup> C. Kittel, *Rev. Mod. Phys.* **21**, 541, 1949.

<sup>7)</sup> The "effective exchange" energy describes formally the tendency for parallel alignment of magnetic moments on the same sublattice. This tendency originates from the actually existing negative superexchange interaction between magnetic moments on different sublattices (cf. part III).



in table I<sup>8)</sup>). The equation for spheres of diameter  $d_0$  reads roughly<sup>6)</sup>:

$$\frac{1}{4} \cdot \frac{1}{3} \cdot \frac{J_s^2}{\mu_0} \cdot \frac{4\pi}{3} \cdot \frac{d_0^3}{8} = \frac{\pi d_0^2}{4} \sigma_w$$

$$\left[ \frac{1}{4} \cdot \left( \frac{4\pi}{3} \right) \cdot \frac{d_0^3}{8} J_s^2 = \frac{\pi d_0^2}{4} \sigma_w \right],$$

from which follows:

$$d_0 = \frac{18\sigma_w\mu_0}{J_s^2} \left[ d_0 = \frac{9\sigma_w}{2\pi J_s^2} \right].$$

If the expression for the wall energy  $\sigma_w$  is substituted<sup>9)</sup> one arrives at:

$$d_0 = 36\pi\mu_0 \frac{\sqrt{K}}{J_s} \sqrt{\frac{kT_c}{aJ_0^2}} \left[ d_0 = \frac{9\sqrt{K}}{J_s} \cdot \sqrt{\frac{kT_c}{aJ_0^2}} \right]. \quad (3)$$

Here  $K$  is the anisotropy constant, and  $a$  the mean distance between neighbouring ions belonging to equivalent sublattices (cf. part III).

In the expression (3) for  $d_0$  only the factor  $\sqrt{K}/J_s$  is temperature-dependent. It follows from fig. 4, which gives this quantity for  $\text{BaFe}_{12}\text{O}_{19}$  as a function of temperature, that the critical diameter for  $\text{BaFe}_{12}\text{O}_{19}$  increases with temperature up to a region near the Curie point. This behaviour is different from that of most traditional materials, for which  $\sqrt{K}/J_s$  decreases with temperature. The increase with temperature of  $d_0$  means that at a given field strength in an aggregate of  $\text{BaFe}_{12}\text{O}_{19}$  crystals a smaller number of Bloch walls will be present at higher temperatures and that especially those Bloch walls disappear which have the highest

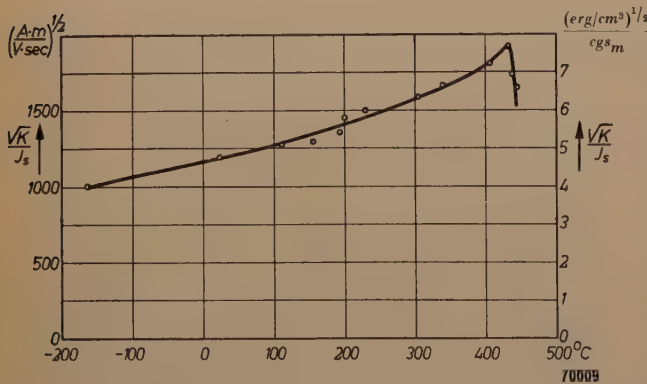


Fig. 4. The quantity  $\sqrt{K}/J_s$  as a function of temperature for  $\text{BaFe}_{12}\text{O}_{19}$ .

<sup>8)</sup> The comparison with iron can be of qualitative value only as equations (1) and (2) are strictly speaking not applicable to the case of iron, which has a cubic magnetic crystal anisotropy. See also note <sup>3)</sup>.

<sup>9)</sup> The expression given in reference <sup>6)</sup> has been altered by taking into account that the exchange energy varies with temperature as  $J_s^2/J_0^2$ .

energy and can therefore be most easily moved by an external field. Considering the mobility of one particular Bloch wall in a crystal that is imperfect due to inclusions and lattice defects as well as due to internal tensions the following must be borne in mind. The force driving the wall is proportional to the magnetization  $J_s$  on which the external field acts, and the resistance against the movement of a wall is due to local variations of the wall energy

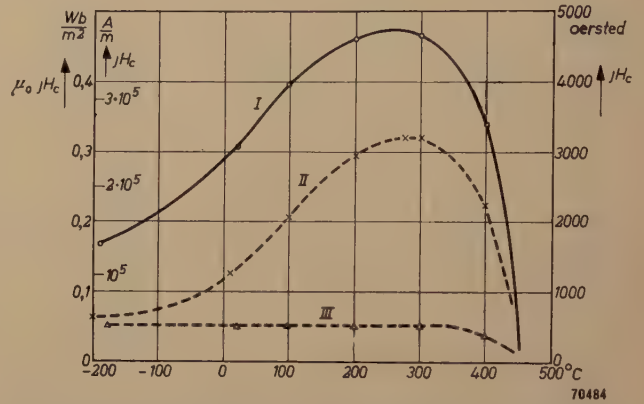


Fig. 5. Coercive force  $JH_c$  as a function of temperature. The drawn line applies to a very fine-grained sintered specimen of  $\text{BaFe}_{12}\text{O}_{19}$ , the broken lines to samples which contain larger crystals. In the latter cases the actual values of the coercive force are 10 times smaller than is read on the scale. The lowest curve was found for a very coarse grained sample of Ferroxdure (largest extension of crystals several mm's).

and increases with the energy of anisotropy and the intensity of magnetization. It thus follows that the mobility of one particular wall in an external field depends on temperature as  $K^{-1/2}$  (fig. 2). Obviously the model of isolated spheres is not strictly applicable to Ferroxdure. However, Ferroxdure is a sintered material, the density of which is about 10% below that calculated for the case of the absence of pores (X-ray-value)<sup>10)</sup>. We believe that the interplay of the decrease of the number of walls and the increase of the mobility of a particular wall with temperature is mainly responsible for the maximum in the curve of the coercive force  $JH_c$  vs temperature as shown in fig. 5.

As to the actual crystal size for which wall formation can be avoided and accordingly a high coercive force can be obtained, it is seen from table II, that the rough calculation arrives at dimensions of about one micron. It has been verified experimentally by grinding a coarse-grained polycrystal-

<sup>10)</sup> Calculated by dividing the weight of the unit cell by its volume,  $(2W_m/N_A)/\frac{1}{2}ca^2/\sqrt{3}$ , where  $c$  is the cell dimension along the  $c$ -axis,  $a$  is the cell dimension along the  $a$ -axis,  $W_m$  is the molecular weight and  $N_A$  is Avogadro's number.



line sample of Ferroxdure of approximate composition  $\text{BaFe}_{12}\text{O}_{19}$  to different grain sizes (cf. *table III*) that the coercive force at room temperature increases rapidly when dimensions of one micron are approached.

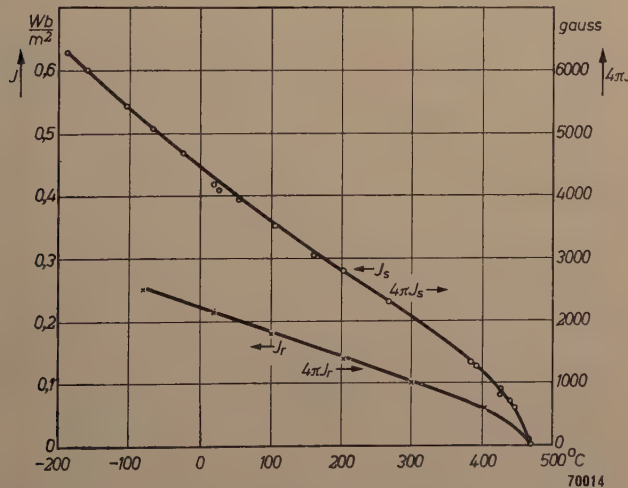
**Table III.** Coercive force of Ferroxdure for various grain sizes.

	$\mu_0 J H_c$ in $\text{Wb/m}^2$	$[J H_c]$ [Oe]
polycrystalline specimen; crystal diameter $> 300 \mu$	0.0050	[50]
specimen ground; diameter of particles about $100 \mu$	0.0075	[75]
specimen ground; diameter of particles about $3 \mu$	0.1240	[1240]

In sintered specimens of  $\text{BaFe}_{12}\text{O}_{19}$  the largest coercive forces are obtained in samples which are fired in such a way as to avoid as much as possible the growth of large crystals.

Remanence

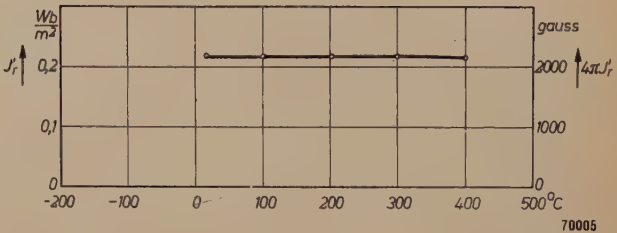
The remanent magnetization of a hard magnetic material consisting of crystals with one direction of easy magnetization oriented at random should be one half of the saturation magnetization. This has been found to be true for sintered Ferroxdure of the approximate composition  $\text{BaFe}_{12}\text{O}_{19}$  at temperatures up to  $400^\circ\text{C}$ , as can be seen from *fig. 6*.



**Fig. 6.** The remanent magnetization  $J_r$  of sintered Ferroxdure of the approximate composition  $\text{BaFe}_{12}\text{O}_{19}$  and the saturation magnetization  $J_s$  of  $\text{BaFe}_{12}\text{O}_{19}$  of about the same density as functions of temperature. Note that the relation  $J_r = \frac{1}{2} J_s$  holds well.

The value of the remanent induction  $B_r = J_r = \rho \sigma_r$  [ $B_r = 4\pi J_r = 4\pi \rho \sigma_r$ ] depends on the apparent density ( $\rho$ ) of the material. (In this formula  $\sigma_r$  is the saturation magnetic moment per unit mass in  $\text{Wb m/kg}$  [ $\text{gauss cm}^3/\text{gram}$ ] and hence independent

of the density.) The X-ray density <sup>10)</sup> of the material is  $5300 \text{ kg/m}^3$  [ $5.3 \text{ g/cm}^3$ ] and the highest induction would be obtained with material having this maximum density. This density, however, cannot be obtained without the growth of crystals appreciably larger than one micron, so that the highest remanent induction can only be obtained at the cost of a lower coercive force and vice versa. Therefore a compromise is sought and the density is kept below  $5300 \text{ kg/m}^3$  [ $5.3 \text{ g/cm}^3$ ].



**Fig. 7.** Remanent magnetization at room temperature  $J_r'$  of a sample of Ferroxdure which starting from the remanent state at room temperature has been heated to a temperature plotted as abscissa and cooled to room temperature again.

Owing to the very high coercive force at elevated temperatures, i.e.: the high resistance to demagnetization, the remanent magnetization of a rod of Ferroxdure generally returns to its original value after heating to temperatures up to  $400^\circ\text{C}$ . *Fig. 7* shows the remanent induction of a rod with demagnetization factor  $N=0.008$  [ $N'=0,1$ ] which was magnetized at room temperature, then heated to the temperature plotted as abscissa and measured at room temperature. During and after the heat treatment it was not exposed to a magnetic field except its own demagnetizing field. Thus the remanence can be varied reversibly by a factor 4 (see *fig. 6* and *7*) by varying the temperature between between  $20^\circ\text{C}$  and  $400^\circ\text{C}$ . This effect can be utilized in temperature measuring and regulating devices, provided the demagnetizing factor is not too large.

Demagnetization curve and value of  $(BH)_{\text{max}}$

*Fig. 8* shows the  $B$ - $H$  curve for a material with fairly large values of the coercive forces  $JH_c$  and  $BH_c$ . In *fig. 9* the remanent induction is plotted as a function of a demagnetizing field which is applied and removed before measurement. It is seen that demagnetizing fields up to  $\mu_0 H = 0.16 \text{ Wb/m}^2$  [ $H = 1600$  oersted] do not lower the remanence by more than 1%. As a consequence Ferroxdure magnets can be magnetized outside the magnetic circuit in which they are to be used, notwithstanding the fact that they are thus exposed to stronger demagnetizing fields.



The  $(BH)_{\max}$  values for Ferroxdure lie in the range of  $6400\text{--}7200\text{ J/m}^3$  [ $0.8 \times 10^6\text{--}0.9 \times 10^6$  gauss Oe]. These values are not large in comparison with e.g. those for "Ticonal" G with  $(BH)_{\max}$  values up to  $45\,800\text{ J/m}^3$  [ $5.7 \times 10^6$  gauss Oe]. However, as was already mentioned in part I, the  $(BH)_{\max}$  value should not be used without some reserve as a criterion for the volume of permanent magnet material necessary to obtain a given field strength in an air gap of given volume. This is due to the fact that the demagnetizing field caused by an air gap (and thus also the stray field) depends on the magnetic permeability of the permanent magnet material, the demagnetizing field being stronger the higher the permeability. As the relative permeability of Ferroxdure is only about 1, as against a value of

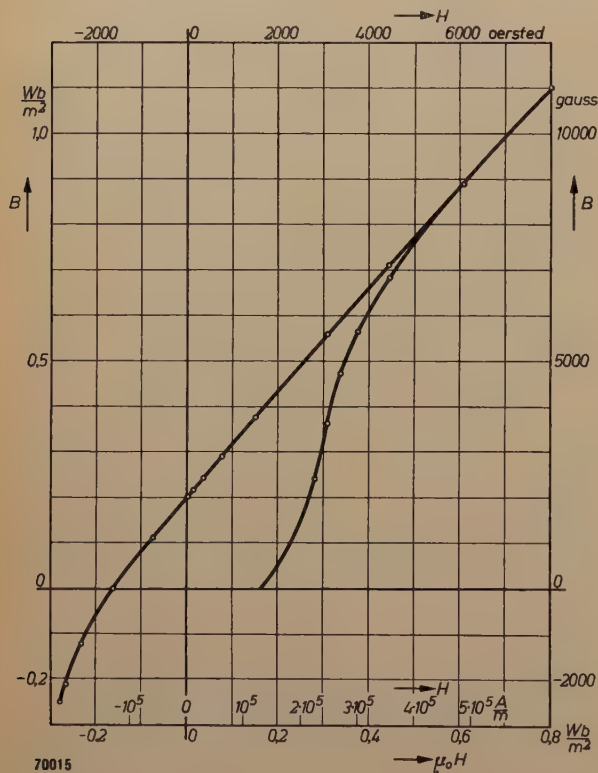


Fig. 8. Magnetization curve ( $B$ - $H$  curve) for Ferroxdure.

about 4 for "Ticonal", Ferroxdure compares more favourably with "Ticonal" G than is apparent from the comparison of the  $(BH)_{\max}$  values. The working point of the material shown in fig. 8 (corresponding to  $(BH)_{\max} = 6650\text{ J/m}^3$  [ $0.83 \times 10^6$  gauss oersted]) is  $B = 0.0925\text{ Wb/m}^2$  [925 gauss],  $\mu_0 H = -0.09\text{ Wb/m}^2$  [ $H = -900\text{ Oe}$ ].

Owing to the rather low remanent induction together with the very high coercive force of Ferroxdure, the design of a magnetic circuit with this material will be quite different from that for traditional materials. The permanent magnet in a Ferroxdure circuit has to be disc-shaped (see fig. 2

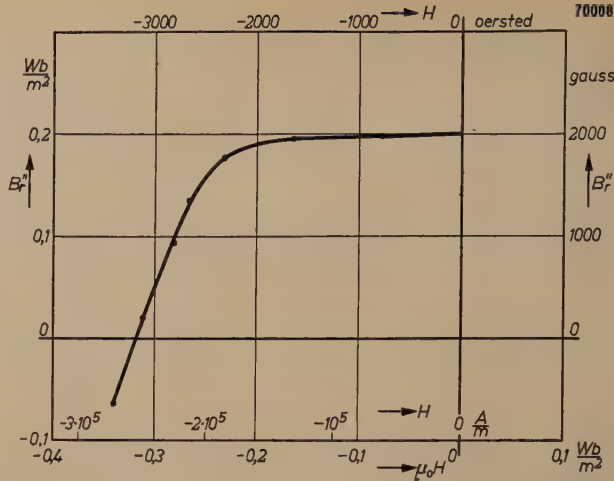


Fig. 9. Remanent induction  $B_r''$  of a sample of Ferroxdure which, starting from the remanent state, has been subjected to a demagnetizing field  $H$  during some time.

of part I), while in circuits using traditional materials generally a more rod-shaped magnet has to be used. For certain loudspeaker circuits this proved to be no disadvantage, since the loudspeaker cone itself has a certain lateral extension.

Electric resistivity

The results of measurements of the resistivity of Ferroxdure as a function of temperature are reproduced in fig. 10<sup>12)</sup>. The electric resistivity of Ferroxdure can be seen to be very large, larger than  $10^6\text{ }\Omega\text{m}$  [ $10^8\text{ }\Omega\text{cm}$ ] at room temperature. This can be understood from the fact that  $\text{BaFe}_{12}\text{O}_{19}$  contains only trivalent iron ions<sup>11)</sup>.

Ferroxdure will therefore prove to be a very

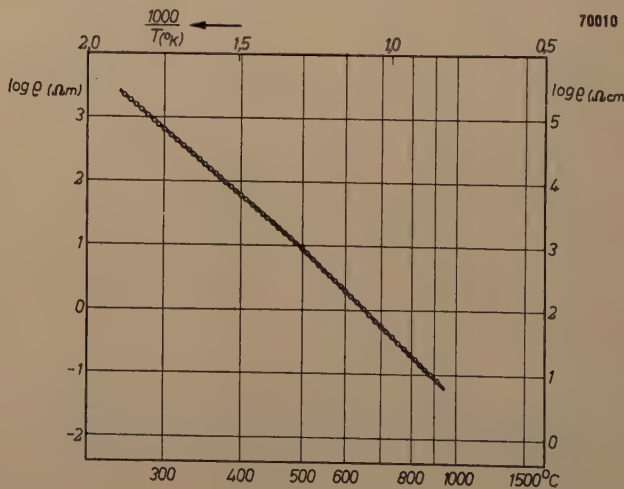


Fig. 10. The logarithm of the resistivity  $\rho$  for Ferroxdure of the approximate composition  $\text{BaFe}_{12}\text{O}_{19}$  as a function of absolute temperature. Plotted is  $\log \rho$  vs  $1000/T$ .

11) J. H. de Boer and E. J. W. Verwey, Proc. Phys. Soc. 49, extra part, 59, 1937.  
12) The measurements were carried out by J. Smit of this laboratory.



suitable material for high frequency applications, especially in combination with Ferroxcube, e.g. in cases where it is desired to subject this material to a polarizing field. One application of a polarizing field is that a low or negative temperature coefficient of the permeability may thus

be obtained (see A and also reference<sup>2</sup>) of part I).

The compound  $\text{BaFe}_{18}\text{O}_{27}$ , which contains both ferric and ferrous ions, shows a much higher conductivity than  $\text{BaFe}_{12}\text{O}_{19}$ .

A summary of the properties of Ferroxdure is given in table IV.

**Table IV.** Some approximate data on Ferroxdure at room temperature. The composition of the essential phase is  $\text{BaFe}_{12}\text{O}_{19}$ . The material, being a sintered ceramic, is brittle and can be ground.

Electric resistivity	$>10^6 \text{ } \Omega\text{m}$ [ $10^8 \text{ } \Omega\text{cm}$ ]
Saturation magnetic moment per unit mass	$8.75 \times 10^{-5} \text{ Wb m/kg}$ [70 gauss $\text{cm}^3/\text{g}$ ]
Density { X-ray value actual value	5300 $\text{kg/m}^3$ [5.3 $\text{g/cm}^3$ ] approx. 4800 $\text{kg/cm}^3$ [approx. 4.8 $\text{g/cm}^3$ ]
Remanent induction	approx. 0.205 $\text{Wb/m}^2$ [approx. 2050 gauss]
$J$ -coercive force $\mu_0 J H_c$ [ $J H_c$ ]	0.24 $\text{Wb/m}^2$ [approx. 2400 Oe]
$B$ -coercive force $\mu_0 B H_c$ [ $B H_c$ ]	approx. 0.145 $\text{Wb/m}^2$ [approx. 1450 Oe]
$(BH)_{\text{max}}$	approx. 6800 $\text{J/m}^3$ [approx. $0.85 \times 10^6$ gauss Oe]
Working point	$B \approx 0.1 \text{ Wb/m}^2$ [ $B \approx 1000$ gauss] $\mu_0 H \approx -0.085 \text{ Wb/m}^2$ [ $H \approx -850$ Oe]
Temperature coefficient of remanent induction	-0.2 % per $^\circ\text{C}$
Temperature coefficient of induction in working point	approx. -0.15 % per $^\circ\text{C}$
Curie temperature	450 $^\circ\text{C}$

### III. SATURATION MAGNETIZATION AND CRYSTAL STRUCTURE

#### General

The saturation magnetization is of great interest from a practical as well as from a more fundamental point of view. Indeed, it has already been mentioned that an important quantity like the remanent magnetization is closely related to the saturation magnetization. As regards the theoretical aspects, from a study of the saturation magnetization it will be possible to get an insight into the mechanism which is responsible for the magnetic behaviour of the oxides which are dealt with. It will be found that this mechanism is completely analogous to that which prevails in the Ferroxcube materials, which were treated in detail in A (cf. I, <sup>1</sup>) (non-compensated antiferromagnetism). Because of this analogy between Ferroxdure and Ferroxcube we shall start with recalling some facts about the latter materials.

Ferroxcube materials are ferromagnetic oxides which chemically belong to the group of cubic ferrites, the crystal structure of which is the so-called spinel structure. In this structure there are two non-equivalent crystallographic positions available for the metal ions, the so-called octahedral and tetrahedral sites, which form the octahedral and tetrahedral sublattices respectively. The inter-

action<sup>3</sup> between two magnetic ions is dependent on the kind of sites they occupy. So even if a ferrite with only one kind of magnetic ions (situated on both sublattices) is considered, one has to distinguish between three different interactions, which we shall call briefly: tetrahedral - tetrahedral, tetrahedral-octahedral and octahedral - octahedral interactions, meaning the interaction between a magnetic moment on a tetrahedral site with another one on a tetrahedral site etc. Néel was the first to point out the importance of these three interactions and he generalized the existing "molecular field" theory of ferromagnetism for the case of these different interactions<sup>1</sup>). From the experimental data regarding the values of the saturation magnetization at zero absolute temperature<sup>2</sup>) and regarding the temperature dependence of the paramagnetic susceptibility above the Curie point  $\chi = J/\mu_0 H = \mu_r - 1$  [ $\chi = J/H = (\mu - 1)/4\pi$ ] Néel deduced that a strong tendency exists for anti-

<sup>1</sup>) L. Néel, Ann. Physique **3**, 137, 1948.

<sup>2</sup>) In this part when speaking of the saturation magnetization we always mean the saturation magnetization at zero absolute temperature.



parallel alignment of magnetic moments on neighbouring non-equivalent sites and a much weaker tendency for antiparallel alignment of magnetic moments on neighbouring equivalent sites. In order to explain roughly the value of the saturation magnetization of most of the single ferrites, for which the conditions are most simple, it is sufficient to take into account the predominant negative tetrahedral-octahedral interaction only. We thus obtain in this simple case for the value of the saturation moment  $M_s$  expressed in Bohr magnetons per molecule the formula:

$$M_s = (M_s)_{\text{tetr}} - (M_s)_{\text{oct}},$$

where  $(M_s)_{\text{tetr}}$  and  $(M_s)_{\text{oct}}$  are the sum of all magnetic moments in one "molecule", situated on tetrahedral and octahedral sites respectively. From this the saturation magnetic moment per unit mass in Wb m/kg [gauss cm<sup>3</sup>/gram],  $\sigma_0$ , is found according to the formula:

$$\sigma_0 = \mu_0 \frac{M_s \mu_B N_A}{W_m} \left[ \sigma_0 = \frac{M_s \mu_B N'_A}{W_m} \right], \quad (1)$$

in which  $N_A$  is Avogadro's number,  $\mu_B$  is the value of the Bohr magneton, viz.  $9.27 \times 10^{-24}$  Am<sup>2</sup> [ $9.27 \times 10^{-21}$  erg/gauss] and  $W_m$  is the molecular weight<sup>3)</sup>.

We see from the foregoing that Néel's theory is of a formal character in so far as it presupposes the existence of the interactions between the magnetic moments on the various lattice sites and adjusts the sign and magnitude of the interactions so as to be in accordance with the experiments. However, the mere existence of such interactions can not be understood in a more or less "elementary" way, as these interactions must be fundamentally different from the (positive) interaction between the magnetic moments in a ferromagnetic metal. As is well known, the interaction in these metals, the so-called exchange interaction, is of a short range nature, i.e. it is negligible between magnetic moments which are not on neighbouring sites. However, in the ferrites with spinel structure, the magnetic ions are always more or less separated by large oxygen ions and thus are much too far apart to permit of an appreciable direct exchange interaction. Besides this, the exchange interaction is also impeded by the shielding effect of the oxygen ions.

<sup>3)</sup>  $N_A = 6.025 \times 10^{26}$  molecules per kg molecule,  $N'_A = 6.025 \times 10^{23}$  molecules per gram molecule. The factor  $\mu_0$  may also be suppressed, in which case  $\sigma_0$  is expressed in Am<sup>2</sup>/kg. The two possibilities correspond to the two possible ways of defining a magnetic moment, viz., by a "volume moment"  $m_v$  (energy =  $m_v H$ ) or by an "area moment"  $m_A$  (energy =  $m_A B$ ).

Néel already pointed out that a rather intricate mechanism, proposed by Kramers<sup>4)</sup>, might be responsible for the above-mentioned interactions between two magnetic ions separated by a non-magnetic anion. In this mechanism, called super-exchange, the anions play an essential role. A more quantitative theory based on these ideas was given by Anderson<sup>5)</sup>.

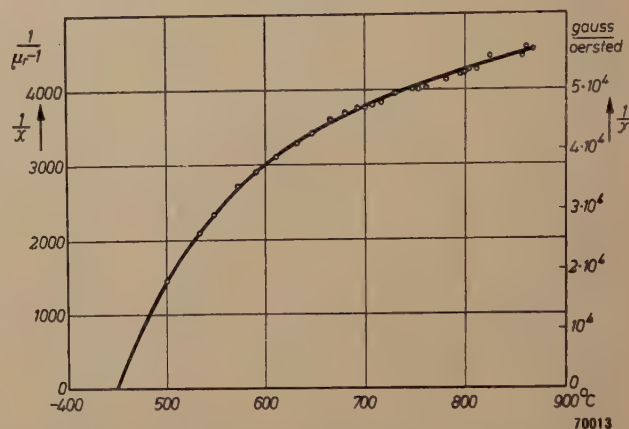


Fig. 1. The reciprocal of the paramagnetic susceptibility  $1/\chi$  of  $\text{BaFe}_{12}\text{O}_{19}$  as a function of temperature. It should be noticed that in a normal ferromagnetic above the Curie point this curve should be a straight line according to the Curie-Weiss law. If a straight line would be drawn tangentially to the  $1/\chi$  vs.  $T$  curve in the Curie point ( $1/\chi = 0$ ) it is seen that  $1/\chi$  is smaller and thus  $\chi$  is larger than if a Curie-Weiss law would hold. This may be made plausible by the assumption that at the Curie point only the weakest interactions lose their ordering influence whereas the stronger interactions still cause a local ordering of the magnetic moments, which is destroyed only at higher temperature. Thus with increasing temperature the number of "free" magnetic moments increases, by which increase the susceptibility falls off more slowly than in a normal ferromagnetic above the Curie point.

Anderson's theory explains the negative sign of the interaction. The theory shows that for given distances between the anion O and the first magnetic ion  $\text{Me}^{(1)}$  and between the anion and the second magnetic ion  $\text{Me}^{(2)}$  the interaction is the larger the nearer the angle  $\text{Me}^{(1)}\text{-O-Me}^{(2)}$  is to  $180^\circ$ . The interaction will be smallest if the angle  $\text{Me}^{(1)}\text{-O-Me}^{(2)}$  is  $90^\circ$ . As regards the dependence of the super-exchange interaction on the distances  $\text{Me}^{(1)}\text{-O}$ ,  $\text{O-Me}^{(2)}$ , it can be said that it will decrease rapidly with increasing distances. If the dependence on distance is taken into account by neglecting interactions involving  $\text{Me-O}$  distances larger than  $3 \text{ \AA}$  one can estimate the strength of the interaction between two magnetic ions from the given angles and distances. Thus a useful rule of thumb is obtained.

<sup>4)</sup> H. A. Kramers, *Physica* **1**, 182-192, 1934.

<sup>5)</sup> P. W. Anderson, *Phys. Rev.* **79**, 705, 1950.



The preponderance of the interactions of magnetic moments on non-equivalent lattice sites in the ferrites can according to this rule be ascribed to the fact that the angle  $\text{Me}_{\text{tetr}}\text{-O-Me}_{\text{oct}}$  is of the order of  $120^\circ$ , whereas the angles  $\text{Me}_{\text{tetr}}\text{-O-Me}_{\text{tetr}}$  and  $\text{Me}_{\text{oct}}\text{-O-Me}_{\text{oct}}$  are of the order of  $80^\circ$  and  $90^\circ$  respectively.

From this it is suggested that also for compounds more complex than the ferrites, it should be possible to determine very roughly the various interactions without an intricate analysis of the experimental data, once the crystal structure (and thus the various angles and distances) of the compound is known and use is made of the above-formulated rule of thumb. In this way it is possible to make an estimate of the saturation magnetization.

The value of the saturation magnetization as well as the temperature dependence of the magnetic susceptibility (fig. 1) of the two oxides to be treated in this part of the paper lend strong support to the assumption that also in these materials there exists a negative super exchange interaction between the magnetic ions.

#### Crystal structure of $\text{BaFe}_{12}\text{O}_{19}$

It was already mentioned that the main component of the permanent magnet material which is available at the moment under the name of Ferroxdure is a ferromagnetic phase with hexagonal symmetry, the formula of which is  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$  or  $\text{BaFe}_{12}\text{O}_{19}$ . It was shown by Adelsköld<sup>6)</sup> that this compound is isomorphous to the mineral magnetoplumbite, which has a composition near to  $\text{Pb}(\text{Fe}, \text{Mn})_{12}\text{O}_{19}$ . The crystal structure of this mineral was determined by the same author and is shown in fig. 2a (see page 207). The structure given here is slightly idealized, i.e. small deviations of the parameters (coordinates of the ions in the unit cell) of the iron and oxygen ions from the simple values used in this figure have been neglected. The figure shows that the oxygen ions form a hexagonal close-packed lattice, some sites of which are occupied by the Ba-ions. The same argument is valid if the Ba-ions are replaced by strontium or lead ions. These three ions have ionic radii which do not differ appreciably from the radius of an oxygen ion. This is shown in the following table.

The ferric ions are found in the interstices of the oxygen lattice, like the metal ions in the spinel structure. A closer inspection of the crystal structure shows that there are five non-equivalent lattice

Table I. Ionic radii according to V.M. Goldschmidt.

ion	radius in Å
$\text{O}^{2-}$	1.32
$\text{Ba}^{2+}$	1.43
$\text{Sr}^{2+}$	1.27
$\text{Pb}^{2+}$	1.32

sites for the ferric ions. In order to be able to calculate the strength of the various interactions from experimental data, one would have to generalize the molecular field theory of ferromagnetism for the case of five sublattices, which would be much too complicated. However, if the crystal structure is known, we can apply our rule of thumb for the strengths of the interactions. In order to facilitate comparison with the spinel structure, which thanks to former publications may be more familiar to our readers, the spinel lattice has been drawn also in a slightly idealized form in fig. 2b, with a vertical orientation of the  $[111]$  direction.

A comparison shows that in these idealized structures a large part of the ionic configuration in the  $\text{BaFe}_{12}\text{O}_{19}$  lattice is identical with that of the spinel lattice, as was already pointed out by Adelsköld. In the layers between these spinel "blocks" the oxygen lattice contains a  $\text{Ba}^{2+}$  ion. In the same layer as the  $\text{Ba}^{2+}$  ion a ferric ion ( $\odot$ ) appears surrounded in an unusual way by a trigonal bipyramid of five oxygen ions.

The ferric ions on octahedrally surrounded sites belong to three different crystallographic positions ( $\odot$ ,  $\otimes$  and  $\oplus$ ) so that together with the tetrahedral position ( $\circ$ ) there are five non-equivalent crystallographic positions as shown in the fig. 2a.

With the aid of our rule of thumb based on Anderson's theory we can now assign a direction (up or down, at  $0^\circ\text{K}$ ) to the magnetic moments of the various ions provided that we arbitrarily fix the direction of the moment of the ion in the  $\odot$  lattice (e.g. up). Now both adjacent moments in the  $\otimes$  lattice will point down. The  $\odot$ -oxygen- $\otimes$  interaction is namely large, because the angle  $\odot$ -oxygen- $\otimes$  is large (of the order of  $140^\circ$ ), whereas the competing  $\otimes$ -oxygen- $\otimes$  interaction, which would tend to orient the  $\otimes$ -moments mutually antiparallel, will be small because the angle  $\otimes$ -oxygen- $\otimes$  is near  $90^\circ$  (of the order of  $80^\circ$ ). Continuing according to this principle we obtain the directions of the moments as given in fig. 2a.

Thus for the complete unit cell 16 moments pointing up and 8 pointing down are found i.e. a resultant spontaneous magnetization of  $16 - 8 = 8$  moments.

<sup>6)</sup> V. Adelsköld, Arkiv för Kemi, Mineralogi och Geologi 12A, No. 29, 1, 1938.



As each ferric ion has a moment of 5 Bohr magnetons, for the saturation magnetic moment  $M_s$  a value of 40 Bohr magnetons per unit cell is obtained, which according to formula (1) is equivalent to  $\sigma_0 = 12.5 \times 10^{-5}$  Wb m/kg [ $100.5 \text{ gauss} \cdot \text{cm}^3/\text{g}$  <sup>7)</sup>]. In fig. 3 the measured values of the saturation moment are plotted against temperature <sup>8)</sup>. By extrapolating this curve towards 0 °K we arrive at a value of  $\sim 13.75 \times 10^{-5}$  Wb m/kg [ $\sim 110 \text{ gauss} \cdot \text{cm}^3/\text{gr}$ ] for the saturation moment at zero temperature, which, given the crude assumptions involved in our rule of thumb and the uncertainty in the extrapolation, is in satisfactory agreement with theory <sup>9)</sup>.

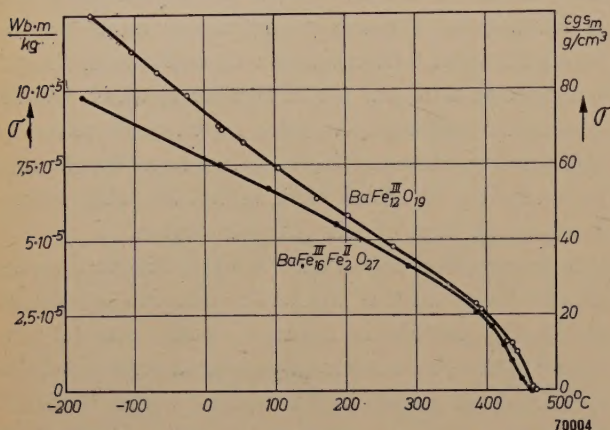


Fig. 3. Saturation magnetic moment  $\sigma$  as a function of temperature.

The low value of the remanent magnetization of Ferroxdure can now be understood from a more fundamental point of view as being due to the fact that in this material the magnetic behaviour is determined by the tendency for antiparallel alignment of the ionic magnetic moments, which will always give rise to a rather low saturation magnetization and thus to a low remanent magnetization.

### Crystal structure of $\text{BaFe}_2^{\text{II}}\text{Fe}_{16}^{\text{III}}\text{O}_{27}$

The second oxide that will be considered here and which also is magnetically hard has a crystal structure very similar to that of  $\text{BaFe}_{12}\text{O}_{19}$ .

The chemical composition of this oxide is  $\text{BaO} \cdot 2\text{FeO} \cdot 8\text{Fe}_2\text{O}_3$  or  $\text{BaFe}_2^{\text{II}}\text{Fe}_{16}^{\text{III}}\text{O}_{27}$ . As may be seen from fig. 2c the structure of this compound, which was determined by P. B. Braun of this laboratory <sup>10)</sup>, can also be described as consisting of spinel "blocks" separated by layers containing Ba-ions. These layers are identical with those in the structure of  $\text{BaFe}_{12}\text{O}_{19}$ . The difference between the two structures is that in  $\text{BaFe}_2^{\text{II}}\text{Fe}_{16}^{\text{III}}\text{O}_{27}$  the spinel "blocks" are higher than in  $\text{BaFe}_{12}\text{O}_{19}$  (cf. fig. 2a), because two "molecules" of  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$  (magnetite) are introduced into each block.

The arrangement perpendicular to the hexagonal axis is thereby slightly altered as compared with the arrangement of the analogous ions in  $\text{BaFe}_{12}\text{O}_{19}$ . The position of the ferrous ions cannot be determined by X-rays, but in order to obey the electrostatic valency rule <sup>11)</sup> they should be located somewhere midway between the layers containing barium. Assuming a preference for an octahedral position like in magnetite, they should be situated in  $\odot$  or  $\ominus$  sublattices, both of which have moments pointing up.

Each  $\text{Fe}^{2+}$  ion having a moment of 4 Bohr magnetons the spontaneous magnetization of this oxide obtained with the aid of our rule of thumb is  $(20-12)5 + 4 \times 4 = 56$  Bohr magnetons, or:  $\sigma_0 = 12.4 \times 10^{-5}$  Wb m/kg [ $99.6 \text{ gauss} \cdot \text{cm}^3/\text{g}$ ].

This value should be compared with the experimental value  $\sigma_0 = 10.6 \times 10^{-5}$  Wb m/kg [ $85 \text{ gauss} \cdot \text{cm}^3/\text{g}$ ].

An illustration of the striking sensibility of the magnetic behaviour to changes in the crystal structure and an additional confirmation of the usefulness of our rule of thumb can be given by considering yet another compound.

A potassium compound exists with the formula  $\text{K}_2\text{O} \cdot 11\text{Fe}_2\text{O}_3$  or  $\text{KFe}_{11}\text{O}_{17}$ , which has a crystal structure very similar to that of  $\text{BaFe}_{12}\text{O}_{19}$ . This compound, however, is non-ferromagnetic, even at very low temperatures.

The crystal structure, given in fig. 2d, was proved by Adelsköld to be the same as that of  $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  or  $\text{NaAl}_{11}\text{O}_{17}$  (the so-called " $\beta$ -alumina"), the structure of which was determined by Beever and Ross <sup>12)</sup>. The lattice is identical with that of  $\text{BaFe}_{12}\text{O}_{19}$  except for the arrangement in the layer containing the large ion i.e. the Ba resp. K ion. In  $\text{KFe}_{11}\text{O}_{17}$  the  $\odot$  position is unoccupied and the three oxygen ions present in the  $\text{BaFe}_{12}\text{O}_{19}$  structure have been replaced here by one oxygen ion situated midway between the ferric ions in the  $\ominus$  positions. This slight difference in structure explains the large difference in magnetic behaviour. In fact, in

<sup>7)</sup> In applying formula (1) it should be taken into account that one unit cell of  $\text{BaFe}_{12}\text{O}_{19}$  contains two "molecules".

<sup>8)</sup> Since the materials under consideration show an extremely large magnetic anisotropy, a very high field strength is necessary to measure the saturation magnetization in a direction of difficult magnetization. Therefore small single crystals were taken, which were measured in the direction of easy magnetization. The measurements were performed with an apparatus described in reference <sup>1)</sup> of part II. The error is of the order of two percent.

<sup>9)</sup> In making the extrapolation one should take into account that according to Nernst's theorem the slope of the magnetization vs. temperature curve has to become zero near 0 °K.

<sup>10)</sup> The results of this determination will be published in greater detail elsewhere.

<sup>11)</sup> In a stable ionic structure the valency of each anion is exactly or nearly equal, with opposite sign, to the sum of the electrostatic bonds to it from the adjacent cations.

<sup>12)</sup> C. A. Beever and M. A. S. Ross, Z. Kristallogr. **97**, 57, 1937.



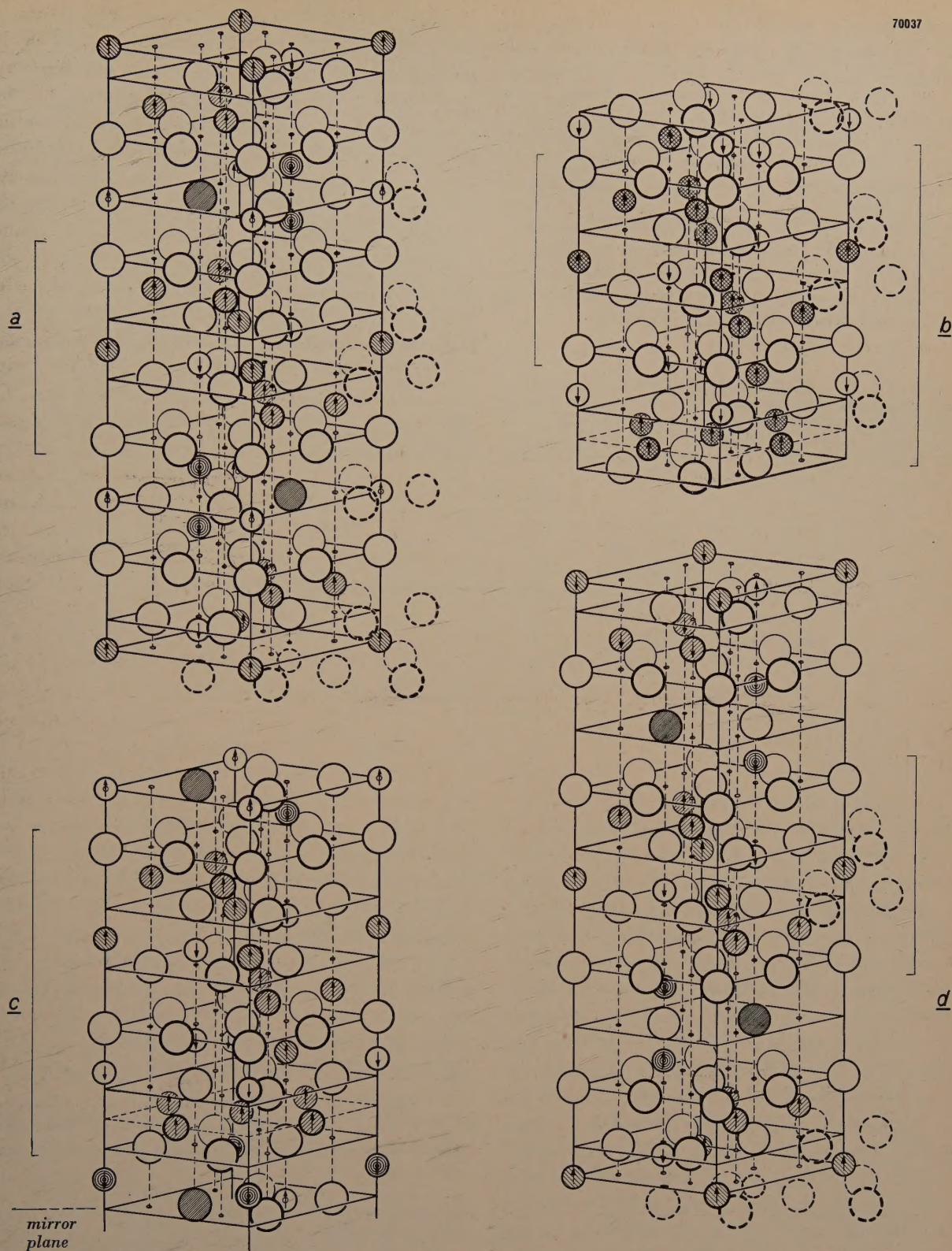


Fig. 2. a) Crystal structure of  $\text{BaFe}_{12}\text{O}_{19}$ .

b) Spinel structure, with a vertical orientation of the  $[111]$  direction.

c) Crystal structure of  $\text{BaFe}_2^{\text{II}}\text{Fe}_{16}^{\text{III}}\text{O}_{27}$  (only half of the unit cell, which possesses a mirror plane, is shown).

d) Crystal structure of  $\text{KFe}_{11}\text{O}_{17}$ .

The large unhatched spheres are the oxygen ions, the large hatched ones are the Ba or K ions. The small spheres are the Fe ions: these are hatched in different ways in order to indicate the different crystallographic positions. All the structures are slightly idealized. In parts of the structures *a*, *c*, *d* the positions of the ions are identical to those in the spinel structure *b*. Such parts are indicated by long brackets. The arrows indicate the direction of the magnetic moment of the ions, the direction for one arbitrary ion in each structure being supposed to point upwards.



$\text{BaFe}_{12}\text{O}_{19}$  the predominant  $\odot$ -oxygen- $\odot$  interactions caused the moments in the  $\odot$  lattices to be parallel; in  $\text{KFe}_{11}\text{O}_{17}$  because the  $\odot$  lattice is empty only the  $\odot$ -oxygen- $\odot$  interaction has to be considered, and as the angle is  $180^\circ$ , this interaction will be strong. The result is that the layer containing the K-ion will be a mirror plane for the directions of the magnetic moments, and the resultant moment of each half unit cell will be cancelled by that of the other half unit cell.

The result is an antiferromagnetic behaviour, in accordance with experiment. The antiferromagnetic Curie temperature may be expected to be very near to the Curie temperature of  $\text{BaFe}_{12}\text{O}_{19}$ . Experimental indications supporting this conclusion have been found.

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**Summary of parts I, II, III.** The material manufactured at present under the name of Ferroxdure is an oxidic ceramic material of the approximate composition  $\text{BaFe}_{12}\text{O}_{19}$ . It is a magnetically hard material which does not contain any cobalt or nickel and which thus offers great economic ad-

vantages. It is characterized by possessing an extremely high value of the coercive force and rather low remanence and saturation magnetization. The extremely high value of the coercive force is due to a large crystal anisotropy. The combination of the two properties, large coercive force and low saturation magnetization means that the material has a large resistance to demagnetization and thus is very well suited for applications where a large resistance to demagnetization is of importance. In the second place these properties open new ways for the design of permanent magnets. The  $(BH)_{\text{max}}$  value of Ferroxdure is rather low. Its specific electric resistivity is high so that it is very well suited for high frequency applications.

The low value of the saturation magnetization and of the remanent magnetization can be understood to be due to the fact that the mechanism which determines the magnetic behaviour of Ferroxdure is non-compensated antiferromagnetism. The strength of the various interactions between the magnetic ions can be estimated theoretically if the crystal structure is known in detail and if use is made of a rule of thumb, based on Anderson's theory of superexchange interaction. In this way the value of the saturation magnetization of Ferroxdure can be estimated and it is shown that the theoretical value thus obtained does not differ much from the value obtained from experiment.

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